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Surface Modification of Titanium and Titanium Alloys: Technologies, Developments, and Future Interests

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Thanks to a considerable number of fascinating properties, titanium (Ti) and Ti alloys play important roles in a variety of industrial sectors. However, Ti and Ti alloys could not satisfy all industrial requirements; the degradation of Ti and Ti alloys always commences on their surfaces in service, which declines the performances of Ti workpieces. Therefore, with aim to further improve their mechanical, corrosion and biological properties, surface modification is often required for Ti and Ti alloys. This article reviews the technologies and recent developments of surface-modification methods with respect to Ti and Ti alloys, including mechanical, physical, chemical, and biochemical technologies. Conventional methods have limited improvement in the properties and/or restriction on the geometry of workpieces. Therefore, many advanced surface-modification technologies have emerged in recent decades. New methods make Ti and Ti alloys have better performance and extended applications. With requirement of high surface properties in future. Understanding the mechanism in various surface-modification methods, combining the advantages of current technologies and developing new coating materials with high performance are required urgently. As such, incorporation of different surface-modification technologies with high-performance modified layers may be the mainstream of surface modifications for Ti and Ti alloys.

1. Introduction

1.1. Titanium and Titanium Alloys

The discovery of titanium (Ti) can be traced up to 1791. An England priest Gregor found an unknown white metallic oxide (TiO_2) in black magnetite.[1] However, due to the significant activity of element Ti, Ti could hardly be separated from TiO_2. Until 1940, Knoll developed an improved method to reduce Ti from TiO_2 by magnesium (Mg), which becomes a common way for industrial manufacturing.[2,3] Ti has an atomic number of 22 and an atomic weight of 47.9.[4] Compared with other elements, the density of Ti is only 4.51 g cm^{-3}, which is about 56% of steel.[1] The melting point of Ti is 1668 °C, which is about 1000 °C higher than that of aluminum (Al).[5] Similar to zirconium (Zr), metallic Ti exhibits a hexagonal close-packed crystalline structure (HCP, α-Ti) up to a temperature of 883 °C and then transforms to a body-centered cubic crystalline structure (BCC, β-Ti) above this temperature.[6–11] Ti exhibits a considerable number of attractive properties, such as high specific strength (i.e., the ratio between the yield strength and density), high fatigue resistance, high corrosion resistance in many media, complete inertness to body environment, and promising biocompatibility. Therefore, Ti and its alloys are commonly regarded as space metals, marine metals, and biological metals.[12–21]

Different types of Ti alloys can be produced when other elements are alloyed with Ti and these Ti alloys exhibit comparable or even better properties compared with commercial pure Ti (CP–Ti), resulting in varied target applications.[22–25] On the basis of their chemical compositions and phase constituents, Ti alloys can be generally classified into α-type Ti alloys, near α-type Ti alloys, (α + β)-type Ti alloys, near β-type Ti alloys, β-type Ti alloys, and Ti-based shape-memory alloys.[12,20,26–30] α-type and near α-type Ti alloys, which mainly contain α-stabilizers (e.g., Al, O, N, C), have admired weldability, castability, and structure stability but limited low-temperature strength and plasticity.[20,27,31] In comparison, (α + β)-Ti alloys, containing a certain quantity of β-stabilizers (e.g., V, Mo, Ta, Nb), display a dual-phase microstructure (5–30 vol% β phase) at the room temperature.[29,32–34] This type of Ti alloys exhibit higher strength compared with α-type or near α-type Ti alloys.[35] (α + β)-Ti alloys can be further strengthened by heat treatment, resulting in the enhanced performance in a wider range of temperature. β-type and near β-type Ti alloys contain higher amount of β-stabilizers, hence they are mainly composed of β phase.[30,36,37] Meanwhile, β-type Ti alloys exhibit lower elastic moduli, excellent corrosion resistance, comparable strength, and even better biocompatibility compared with other

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types of Ti alloys.[19,37–45] The first developed Ti-based shape-memory alloy is near-equiatomic TiNi alloy which has superelasticity and shape-memory effect.[46–48] Such properties of TiNi alloy result from the reversible martensitic transformation. To further demonstrate the advantages of TiNi alloy, many other elements, such as Ag, Zr, Nb, Sn and so on, are added to the conventional TiNi alloy.[48–52] Therefore, TiNiAg, TiZr, TiNbSn, TiNbZrTa, and other Ti-based shape-memory alloys emerged later on.[49–53] **Table 1** summarizes the mechanical properties and corrosion potentials of bulk CP–Ti and some Ti alloys. CP–Ti and $(\alpha + \beta)$-type Ti alloys (e.g., Ti–6Al–4V, Ti–6Al–7Nb, Ti–5Al–2.5Fe, and Ti–3Al–2.5V) are commonly used in aerospace and biomedical industries. Some newly developed β-type Ti alloys with nontoxic elements are also selected to show their properties, which are considered as the candidate alloys to substitute $(\alpha + \beta)$-type Ti alloys. Ti–Ni serials alloys exhibit superelasticity and shape-memory effects and have been used in various fields.[54] Due to their fascinating properties, Ti and Ti alloys can be universally applied in a wide range of industrial sectors.

1.2. Various Applications of Ti and Ti Alloys

Since 1950s, Ti, Ti alloys, and even Ti-based composites have become an important type of structural materials, leading to extensive industrial applications in aerospace, marine, chemical engineering, biomedicine, etc.[6,71–79] In aerospace industry, Ti alloys with the properties of high strength, flame retardation, and damage tolerance are commonly used.[76,80–84] For example, Ti–6Al–4V (in wt%; the same hereafter), which is the first successfully developed Ti alloy, has been widely used for aerospace purposes for its attractive combined performance in strength, plasticity, toughness, and heat resistance.[84] The annealed Ti–6Al–4V exhibits an ultimate tensile strength of about 895–930 MPa and plasticity of 6–10%.[6] Ti–10V–2Fe–3Al (Ti–1023) exhibits excellent forging performance, high ultimate tensile strength, and high damage tolerance.[85] Therefore, Boeing Company first used Ti–1023 in the undercarriages of Boeing-series aircrafts, leading to a significant reduction in their weight. To satisfy the demands for high-temperature applications, Ti–6Al–2Sn–4Zr–2Mo–0.1Si (Ti–6242S) was developed in 1960s. The maximum service temperature of Ti–6242S reaches 540 °C, resulting in being mainly used in engine parts and hot end parts of aircrafts.[86] Ti–5.8Al–4Sn–3.5Zr–0.7Nb–0.5Mo–0.35Si (IMI834), which was developed in 1984, had further higher maximum service temperature (600 °C) of Ti alloys.[87] IMI834 has also being used in the engine parts of Trent 700 and 800 in Boeing 777.[87] Afterward, Ti–6.2Al–2Sn–3.6Zr–0.7Mo–0.1Y–5.0W–0.5Si (BT36) and Ti–5.8Al–4.8Sn–2.0Zr–1.0Mo–0.35Si-0.85Nd (Ti60) were found to have the highest working temperature (about 600 °C).[88,89] However, their creep resistance and high-temperature oxidation resistance rapidly decreased when the working temperature is above 600 °C. Therefore, it is of importance to develop new Ti alloys with better high-temperature performance or to develop a method to resist the ingression of heat for Ti alloys in a high-temperature environment.

The use as biomedical materials is another important application field for Ti and Ti alloys. Generally, stainless steels, Co–Cr alloys and Ti alloys are most frequently used metallic biomedical materials.[64,90–95] For these metallic biomedical materials, elastic modulus is one of critical considerations. If the implant material used has a significantly higher elastic modulus compared with the bone to be replaced, the applied stress is mostly sustained in the implant and cannot be effectively transferred to the adjacent bone tissues (e.g., hip and knee), which can cause bone resorption around the implant, thereby leading to the death of bone cells. This phenomenon is called as "stress shielding effect".[96] Although these metallic biomedical materials exhibit higher elastic moduli than human bone tissues, Ti alloys have lower elastic moduli compared with stainless steels and Co–Cr alloys, which can effectively reduce the stress-shielding effect of the implant after a long-term implantation.[6] Meanwhile, it

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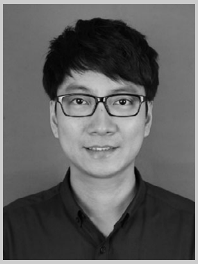

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Table 1. Mechanical properties and corrosion potentials of CP–Ti and some Ti alloys. E is elastic modulus, σ_y is yield strength, and σ_{max} is ultimate compressive/tensile strength.

Alloy	Phase constituent	σ_y [MPa]	σ_{max} [MPa]	E [GPa]	Corrosion potential [V]	Ref.
CP–Ti grade 1	α	170$^{t)}$	240$^{t)}$	105	−0.3$^{a)}$	[6,55]
CP–Ti grade 2	α	275$^{t)}$	345$^{t)}$	105	−0.2–0.2$^{a)}$	[6,56]
CP–Ti grade 3	α	380$^{t)}$	445$^{t)}$	105	–	[6]
CP–Ti grade 4	α	480$^{t)}$	550$^{t)}$	105	–	[6]
Ti–6Al–4V	α + β	825–869$^{t)}$	895–930$^{t)}$	110–114	−0.4$^{a)}$	[29,35]
					−0.22$^{b)}$	[57]
					−0.41$^{c)}$	[58]
Ti–6Al–7Nb	α + β	795$^{t)}$	860$^{t)}$	105	0.3$^{c)}$	[35,58]
					−0.5–1.0$^{d)}$	[59]
Ti–5Al–2.5Fe	α + β	820$^{t)}$	900$^{t)}$	110	−0.5$^{c)}$	[35,60]
Ti–3Al–2.5V	α + β	585$^{t)}$	690$^{t)}$	100	–	[35]
Ti–11Nb–0.5Fe	α + β	796$^{t)}$	1300$^{t)}$	109	–	[35]
Ti–11Nb–3.5Fe	α + β	932$^{t)}$	1600$^{t)}$	101	–	[35]
Ti–8Fe	α″ + β	1562$^{t)}$	1750$^{t)}$	127	–	[35]
Ti–1Nb–7Fe	α″ + β	1785$^{v)}$	1972 ± 12$^{v)}$	124	–	[61]
Ti–9Nb–7Fe	α″ + β	1010$^{v)}$	2007 ± 15$^{v)}$	89	–	[61]
Ti–13Nb–13Zr	β	836–908$^{t)}$	973–1037$^{t)}$	79–84	0.2$^{b)}$	[6,62]
Ti–10Mo–20Nb	β	–	1060 ± 30$^{t)}$	101 ± 2	−0.93$^{b)}$	[57]
Ti–12Mo–13Nb	β	–	1110 ± 10$^{t)}$	84 ± 5	−0.28$^{b)}$	[57]
Ti–12Mo–6Zr–2Fe	β	1000–1060$^{t)}$	1060–1100$^{t)}$	74–85	–	[6]
Ti–15Mo	β	544$^{t)}$	874$^{t)}$	78	−0.25–0.25$^{e)}$	[35,63]
Ti–24Nb–4Zr–8Sn	β	563–700$^{t)}$	665–830$^{t)}$	46–55	−0.25$^{c)}$	[19,64]
Ti–15Mo–5Zr–3Al	β	838$^{t)}$	852$^{t)}$	80	–	[6]
Ti–16Nb–10Hf	β	736$^{t)}$	851$^{t)}$	81	–	[6]
Ti–35.5Nb–7.3Zr–5.7Ta	β	793$^{t)}$	827$^{t)}$	55–66	–	[35]
Ti–29Nb–13Ta–4.6Zr	β	864$^{t)}$	911$^{t)}$	80	–	[35]
Ti–11Nb–7Fe	β	985$^{v)}$	2006$^{v)}$	86	–	[61]
Ti–11Nb–9Fe	β	1078$^{v)}$	–	82	–	[61]
Ti–33Zr–3Fe–2Cr	β	1050$^{v)}$	1750$^{v)}$	140	–	[45]
Ti–33Zr–3Fe–4Cr	β	1100$^{v)}$	2000$^{v)}$	130	–	[45]
Ti–25Nb–3Zr–3Mo–2Sn	β	308–592$^{t)}$	622–716$^{t)}$	49	–	[65]
Ti–Ni	–	210–300$^{t)}$	900–1100$^{t)}$	28–41	−0.4$^{c)}$,−0.5$^{d)}$	[66–69]
45.2Ti–49.8Ni–5Nb	–	230$^{t)}$	900$^{t)}$	38	–	[70]

$^{t)}$Tensile test; $^{v)}$Compressive test; $^{a)}$In 3.5 wt% NaCl solution; $^{b)}$In Ringer's solution; $^{c)}$In Hank's solution; $^{d)}$In simulated body fluid; $^{e)}$In 0.15 M NaCl solution.

was reported that the elements such as Cr and Ni contained in stainless steels and Co–Cr alloys may damage the kidney, liver, and blood cells or may cause some skin-related diseases.[6] In contrast, Ti alloys are inert in the human body, rarely resulting in allergy or other symptoms.[97,98] Therefore, Ti alloys have better biocompatibility than stainless steels and Co–Cr alloys.[99–101] Furthermore, Ti and Ti alloys are nonmagnetic metals which are not influenced by electromagnetic field and/or thunderstorm, contributing to the high safety of human body.[102] Based on these aforementioned advantages, Ti and Ti alloys become a better choice for load-bearing biomedical materials. Basically, Ti and Ti alloys are used as orthopedic implants, including the replacements of cortical bones and dental implantation. For example, Ti–6Al–4V exhibits high strength and fatigue resistance, thereby being commonly used as the replacements of femur and thighbone.[103,104] Many nontoxic β-type Ti alloys were developed in 1990s with aim to avoid the detrimental effects of Al and V in Ti–6Al–4V.[100,105,106] Ti–13Nb–13Zr is the first developed and in-service β-type Ti alloy for implant.[107] Generally, β-type Ti alloys have lower elastic moduli and better corrosion resistance compared with α-type and (α + β)-type Ti alloys. Therefore, β-type Ti alloys have had a flourishing development.[108] In contrast, to further reduce the elastic moduli of Ti alloys and to promote the ingrowth of the bone cells, porous Ti alloys prepared by a variety of preparation methods, such as additive manufacturing and powder metallurgy, gradually emerge.[21,109–114] **Table 2** lists the unit cell structure, porosity, and mechanical properties of porous Ti alloys as well as some human bones. It can be found that the porous Ti alloys have the comparative strength and elastic moduli compared with the human bones.

Generally, the materials for marine equipment should satisfy several factors, including high strength, high corrosion resistance in the extracted products of crude oil, and repair with no need of post-welding heat treatment in the sea conditions.[127] As Ti alloys have such required properties, they are also important for marine constructions and used for heat exchanger, hull structures of deep-water equipment, high-pressure vessels, fire-extinguishing systems, etc.[15] Grade 5 (Ti–6Al–4V) and Grade 23 (Ti–6Al–4V ELI, improved by decreasing the contents of interstitial impurities compared with Ti–6Al–4V) are the most commonly used to construct marine objects.[127] PT–3V, 5V, and 37 alloys (Ti–Al–V series pseudo-α Ti alloys) also meet the requirements for marine constructions.[15] Furthermore, due to their combination of physical and chemical properties, Ti and Ti alloys are actively used in many other industries, such as electroplating industry, automobile industry, construction industry, sports equipment, and so on.[128–136] As such, Ti and Ti alloys have been playing an irreplaceable role in national economy and defense. **Table 3** summarizes the applications of Ti and Ti alloys in a variety of industrial sectors.

1.3. Need of Surface Modifications for Ti and Ti Alloys

Due to their fascinating properties, the uses of Ti and Ti alloys have grown in a variety of fields. However, Ti and Ti alloys still have some intrinsic disadvantages. For example, Ti has relatively low hardness, in the range of 150–200 HV.[149] Even after alloyed with other elements, Ti alloys still exhibit low hardness (e.g., Ti–6Al–4V: 290–375 HV; as-cast Ti–Ni: ∼190 HV; as-cast Ti–25Pd–5Cr: ∼260 HV; as-cast Ti–20Cr–0.2Si: ∼320 HV).[35,149–151] Correspondingly, Ti and Ti alloys exhibit relatively low wear resistance, which may easily cause the seizure in service.[152,153] Meanwhile, when the working temperature is higher than 600 °C, Ti and Ti alloys demonstrate a drastic

Table 2. Unit cell structure, porosity, and compressive mechanical properties of porous Ti alloys and some human bones. *E* is elastic modulus, σ_y is yield strength, and σ_{max} is ultimate compressive strength.

Alloy	Unit cell structure	Porosity	σ_y [MPa]	σ_{max} [MPa]	*E* [GPa]	Ref.
Ti–6Al–4V	Diamond structure	≈80%	16.1–22.0	21.0–29.3	0.9–1.6	[115]
Ti–6Al–4V	Diamond crystal lattice	60–87%	11.4–99.7	16.3–118.8	0.4–6.5	[116]
Ti–6Al–4V	Rhombic dodecahedron structure	62–86%	–	12.4–112.8	0.89–6.34	[117]
Ti–6Al–4V	Honeycomb-like structure	66.3 ± 2.1%	–	116 ± 10	2.5 ± 0.5	[118]
Ti–6Al–4V	Hatched structure	60%	49.6–107.5	127.1–148.4	3.9–12.9	[119]
Ti–6Al–4V	Cubic structure	49.75–70.32%	–	7.28–163.02	0.57–2.92	[120]
Ti–6Al–4V	Lattice structures	88.8–94.7%	–	2.21–8.78	0.025–0.21	[121]
Ti–6Al–4V	Solid cellular foam structure	55–82%	–	–	0.75–9.97	[122]
Ti–6Al–4V	Hollow cellular foam structure	55–89%	–	–	0.48–9.77	[122]
Ti–6Al–4V	Stochastic foam structure	90.08–91.65%	–	3.8–4.5	0.19–0.49	[117]
Ti–24Nb–4Zr–8Sn	Rhombic dodecahedron structure	75%	–	46	1.34 ± 0.04	[109]
Ti–24Nb–4Zr–8Sn	G7 structure	70%	–	35 ± 2	0.7 ± 0.1	[40]
Ti–24Nb–4Zr–8Sn	Topology-optimized	75%	–	58	∼2.3	[40]
Femur	Cortical bones	–	–	17.6	194	[123]
Tibia	Cortical bones	–	–	28.0	195	[123]
Lumbar vertebra	Cancellous bones	–	–	2.7–4.6	0.04–0.06	[124]
Tibia head	Cancellous bones	–	–	2.2–3.9	0.02–0.03	[124]
Vertebra	Cancellous bones	–	–	0.9–2.5	0.02–0.07	[125]
Lumbar spine	Cancellous bones	–	–	1.6–2.5	0.02–0.07	[126]

Table 3. Applications of Ti and Ti alloys in industrial sectors.

Industries	Requirements of materials	Applications	Ref.
Aerospace	Engine: high specific strength, high fatigue resistance, good atmospheric corrosion resistance, and good thermostability	Engine: compressor disk, stator blade, rotor blade, combustor outer casing, jet stack, etc.	[76,80,84,137]
	Fuselage: high specific strength and good thermostability	Fuselage: foot rack, aircraft skin, wing rib, hatch door, fastener, pull rod, etc.	[76,80,84,137]
Biomedicine	Nontoxic, high strength, low elastic modulus, high corrosion resistance in human body fluid, good biocompatibility with bone cells and muscle	Orthopedic implant, tooth, cardiac intima, membrane, fixed screw, surgical blade, hemostatic forceps, bone drill, etc.	[6,12,13,20,126,138–142]
Marine	High specific strength, high corrosion resistance in the seawater and marine atmosphere	Deep-water riser, supplying pipe, hull structure of marine equipment, pump, fire extinguishing, high pressure vessel, high-strength flexible fastening, etc.	[14,15,143]
Chemical Engineering	High corrosion resistance in oxidant and neutral media	Heat exchanger, reaction tower, distiller, scrubber, autoclave, pipe, pump, etc.	[127,144,145]
Military	High corrosion resistance and low density	Tailstock, cannon barrel, wheel and caterpillar of tanks, actuating shaft, etc.	[146–148]
Others	Good comprehensive mechanical properties, low density, high corrosion resistance, low linear expansion coefficient	Steam turbine blade, optical instrument, model airplane, sport equipment, decoration, etc.	[130,131,146]

decrease in strength so that they could not withstand the loading in high-temperature environments.[86–89] These disadvantages have restricted further applications of Ti and Ti alloys as structural materials. Furthermore, although Ti and Ti alloys exhibit excellent corrosion resistance and biocompatibility in the human body, the formed passivation films have significantly different chemical compositions compared with the surrounding tissues. Such a difference results in the difficulty in forming fiber capsules around the biomedical implants.[154] Therefore, only mechanical osseointegration, instead of a strong chemical bone bonding, is presented between the Ti implants and surrounding tissues.[154] Moreover, the passivation film may be peeled off and/or dissolved in the human body due to the joint effect of shear force and body fluid.[1] It should be noted that the wear debris or released ions may lead to inflammation in the human body.[1] As such, these disadvantages also restrict the long-term service performance of Ti and Ti alloys as load-bearing hard tissue implants.

During the actual applications, the degradation of Ti and Ti alloys always commences on their surfaces. The corrosion resistance, wear resistance, and biocompatibility of Ti and Ti alloys are significantly influenced by the characteristics of their surface layers. Synthesis of protective or biocompatible layers on the surface of Ti and Ti alloys can ensure their duration and reliability in the service environments. Therefore, various surface-modification methods have been used over the past 50 years to further improve the performance of Ti and Ti alloys.[1,6,155–158] For example, some surface-modified layers exhibit significantly enhanced wear resistance and/or corrosion resistance compared with the untreated Ti and Ti alloys.[159–161] Some other surface-modified layers exhibit extremely low thermal conductivity and therefore they can act as a thermal barrier to reduce the influence of heat on the underlying Ti and Ti alloys.[162,163] Bioactive surface-modified layers may have better cell affinity and/or antibacterial activity.[49,154,164,165] Such functional surface-modified layers expand the applications of Ti and Ti alloys in many industries. Moreover, the preparation methods of various surface-modified layers are also diverse. As such, an overview of surface modifications for Ti and Ti alloys is recommended. In this Review, a brief introduction to the development and multiple applications of Ti and Ti alloys is first presented. Therefore, the necessity of surface modification treatment for Ti and Ti alloys can be deeply understood. Afterward, various conventional surface-modification technologies are introduced because these technologies had played a decisive role in further utilizations of Ti and Ti alloys in the past. Third, many new preparation technologies of Ti and Ti alloys, such as additive manufacturing[65,166–171] and powder metallurgy (for porous structures)[172–175] were developed in the recent decades. Many Ti products may have complex shapes. Hence, in order to obtain the expected performance of such Ti products, advanced surface-modification methods have emerged and are presented in this part. Finally, a comprehensive comparison of surface modifications of Ti and Ti alloys by different technologies and an outlook of their future interests are concluded.

2. Conventional Technologies for Surface Modification

With aim to improve the surface properties of Ti and Ti alloys, various surface-modification technologies have been developed to satisfy the requirements of service environments during the past 50 years. In terms of the formation mechanism of the surface-modified layers, these technologies can be classified into mechanical methods, physical methods, and chemical methods. These methods are introduced in detail in this section.

2.1. Mechanical Methods

To produce the parts made of Ti and Ti alloys from rods or sheets, the materials need to be first machined into a specific geometry and/or dimension. The fresh surface of Ti and Ti alloys may be oxidized rapidly in the ambient environment. Meanwhile, the machining processes are often associated with the cooling agents or lubricants used, which can adhere to the surface of Ti parts (contamination) or lead to a reoxidation process.[176] Machining processes also result in severe plastic deformation in the surface region of Ti parts, which is prone to facilitate crack initiation or stress corrosion.[176] Therefore, to increase the adhesion between the substrate and surface-modified layers in the subsequent processing steps, surface-modification mechanical methods including grinding, polishing, and sandblasting are commonly used to obtain an acceptable surface with a certain roughness or a specific topography and/or get rid of surface contamination or plastic deformation layer.[177–184] Up to date, grinding, polishing, and sandblasting are rarely solely used for the surface modifications of Ti and Ti alloys due to the limited improvement in the surface properties. However, they are always adopted as auxiliary methods to obtain a clear and acceptable surface.

Similar to general machining technologies, grinding and polishing are used to remove the surface layers with contamination/plastic deformation and to reduce the roughness for Ti and Ti alloys. Surface layers can be easily removed by grinding.[180,181] The surface roughness of Ti and Ti alloys would be reduced to some extent or even mirror surface finish depending on the size of the grinding material and antiscuffing paste used.[180,181] It should be noted that the grinding and polishing are also used in other surface-modification methods to obtain a clear surface with a low roughness.[185,186] In comparison, oxide particles (such as corundum and silica sand) are used in sandblasting to shot against the Ti products by air compressor, with aim to obtain a rough surface as well as specific topographies.[182,183] The surface roughness of Ti and Ti alloys induced by sandblasting is dependent on the shape and size of oxide particles and pressure of air during sandblasting.[182,183] The increased surface roughness also increases the surface area and wettability of the materials; therefore, the sandblasting treatment greatly brings activated surfaces. Such activated surfaces are prone to form a strong chemical bonding with the subsequently prepared layers in other chemistry-related surface-modification methods. In comparison to purely mechanical interlocking, chemical bonding resulted from sandblasting often has enhanced bond strength.[187,188] Therefore, sandblasting can also be considered as a method to enhance the bond strength of the Ti substrate and the surface-modified layers. Watanabe et al.[188] found that the sandblasting treatment using the corundum with the size below 250 μm can apparently improve the shear bond strength of polymer-glass composite to cast Ti substrate. Li et al.[189] conducted an in vivo pullout test and demonstrated that the Ti implant with sandblasted surfaces has roughly five times shear strength of the counterpart with a smooth surface.

Shot peening (SP) can be regarded as an evolutionary technology from sandblasting. In this method, sand is replaced by a large number of hard steel (or ceramic) balls in the size of 0.25–1 mm, which are used to hit the surfaces of materials in the velocities of 20–150 $\mathrm{m\,s^{-1}}$ over a short time in a controlled atmosphere.[190–192] This method introduces severe plastic deformation into the surfaces of the processed materials. Therefore, surface-modified layers with refined grains are obtained. Unal et al.[193] analyzed the microstructure of shot-peened CP–Ti and they found that the grains in the surface layer can be refined to 25–80 nm. SP was first used to improve the fatigue resistance of Ti and Ti alloys as well as other metallic materials, which is attributed to the shot-peening-induced compressive stress in the peened surfaces.[194,195] Fortunately, the hardness and wear resistance of shot-peened Ti and Ti alloys are also enhanced.[159,196] In addition to these features, Aparicio et al.[159] investigated the corrosion behavior of peened CP–Ti with different-sized particles; they found that all peened samples have improved corrosion resistance and their corrosion behavior is not only influenced by the surface roughness but also the compressive stress induced in surface. Lee et al.[195] found that SP increases the fretting fatigue life of Ti–6Al–4V in a simulated seawater environment, as shown in **Figure 1**. These findings elucidate that SP is a useful method to improve the surface properties of Ti and Ti alloys, leading to the substantial applications in aerospace, marine, and biomedicine industries.

2.2. Physical Methods

For physical methods, surface-modified layers directly adhere to the Ti substrates with almost no occurrence of chemical reactions. In such a situation, thermal, kinetic, and electrical energy become the dominant factors for the formation of surface-modified layers. Conventional physical methods mainly include thermal spraying and glow discharge plasma treatment.

2.2.1. Thermal Spraying

The thermal spraying technologies, which use metallic powder, ceramic powder, composites or suspensions as feedstocks, can synthesize a variety of coatings according to the requirements of service environments.[197,198] In these technologies, the feedstocks are heated and/or melted to coat the Ti substrates at a significantly high speed (thermal and kinetic energy). The coatings are prepared layer by layer via successive deposition of the softened or melted feedstocks using predefined parameter sets. In general, thermal spraying technologies require an equipment that can produce flame or plasma arc with high-speed gas flow. In line with the energy sources used, common thermal spraying technologies can be primarily categorized into flame spraying,[199,200] plasma spraying,[201–204] high velocity oxygen fuel spraying,[205,206] and other spraying technologies.[207–209] As the flame spraying and high-velocity oxygen fuel spraying use the combustion of fuel as heat resources, the highest temperature of the flame in these two technologies is about 1700–2700 °C.[210] In contrast, plasma spraying uses plasma arc as heat resource that can provide a significant high temperature ranging from 2700 to 11700 °C, which is capable of melting the coating materials with higher melting points (such as

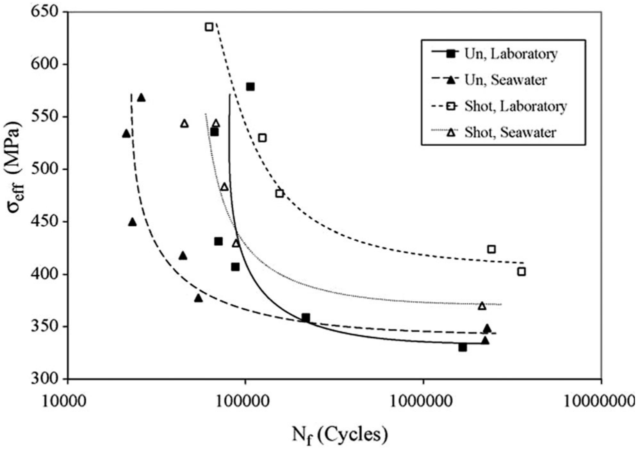

Figure 1. Effective stress (σ_{eff}) versus number of cycles to failure (N_f) for shot-peened Ti–6Al–4V (Shot) and untreated (Un) counterpart under ambient laboratory and seawater environment. (Reproduced with permission.[195] Copyright 2006, Elsevier).

refractory metals and ceramics) on the surface of Ti and Ti alloys.[210]

Irrespective of thermal spraying technologies used, the coated Ti and Ti alloys substantially have better performance than their uncoated counterparts in terms of biocompatibility, wear resistance, and thermal stability. For instance, hydroxyapatite (HA), which exhibits similar mineral phases to the natural hard tissues, has been considered to be used as plasma-sprayed (PS) coating materials on Ti and Ti alloys for biomedical applications since 1975.[1] De Groot et al.[211] reported that the Ti alloy implants with HA coating can strongly bond with bone tissues in a short time. Subsequently, Furlong[212] and Geesink[213] used HA-coated implants of femoral stems as the first clinical trial in 1985 and 1986, respectively. Since then, HA coatings have been widely used in both dental and orthopedic applications. In addition to HA coatings, calcium silicate coatings, such as CaO–SiO_2,[214] $CaSiO_3$ (wollastonite)[215] and CaO–MgO–$2SiO_2$ (dicalcium silicate),[216] were also reported to demonstrate great bioactivity. Liu et al.[217] first used plasma spraying to synthesize a bioactive wollastonite and dicalcium silicate coating on Ti–6Al–4V alloys. After being cultured with osteoblast cells for 4 days, the cells were compact and showed dorsal ruffles. Such a result specifies that PSed wollastonite and dicalcium silicate coatings can promote the proliferation of bone cells; therefore, these coatings exhibit superior bioactivity. Furthermore, fluorapatite, calcium phosphate and their blends were reported to be used as flame- or PSed coating materials on Ti and Ti alloys.[218,219] However, the disadvantage of such bioceramics prepared by thermal spraying is also apparent, e.g., weak bond strength. Generally, the adhesion between the Ti substrate and bioceramics coating is mechanical interlocking. Chemical bonding rarely takes place.[220] Mismatching of thermal expansion coefficients between the Ti substrate and HA often facilitates the formation of tensile forces in the coating and leads to the crack generation and delamination, which finally results in the weak bond strength.[221] Therefore, bond coatings are often used to improve the bond strength of bioceramics coatings. Take TiO_2 as an example, TiO_2 shows a comparable thermal expansion coefficient ($8.7 \times 10^{-6}\,°C^{-1}$) as the Ti substrate ($8.9 \times 10^{-6}\,°C^{-1}$).[221,222] Adding TiO_2 into HA ($15 \times 10^{-6}\,°C^{-1}$) as a component can substantially prevent a steep gradient in the coefficients of thermal expansion between the Ti substrate and outer HA coating.[221,222] In other industrial circles, reactive plasma spraying is a common technology to prepare wear-resistant composite coatings on Ti substrates by depositing pure Ti powder in an N_2-containing gas atmosphere.[223] Ti powder reacts with N_2 during spraying, resulting in the formation of Ti–N compounds in the microstructure of coatings. Hence, the coated Ti alloys reveal significantly better wear resistance than the uncoated counterpart.[223] Such composite coatings can be used in the environments where good corrosion resistance and high wear resistance are demanded. For example, Zhou et al.[162] successfully synthesized thermal-barrier coatings (ZrO_2–8 wt% Y_2O_3) on Ti–6.6Al–3.61Mo–1.69Zr–0.28Si alloy by plasma spraying, which expands the applications of Ti alloys in high-temperature environments.

2.2.2. Glow Discharge Plasma Treatment

Glow discharge plasma treatment is an old method that exposes Ti and Ti alloys to a low-pressure glow discharge (partially ionized gas) to obtain a specific surface with some expected properties; this treatment is carried out in a ultra-high vacuum ($<10^{-7}$ Pa) by applying a high potential difference (about 1 kV, direct current or alternative current) between two electrodes.[224] The processed materials are always at negative potentials. Therefore, the processed materials are impacted by partially ionized gas (e.g., positive ions, negative ions, free electrons, and gas molecules). The universal glow discharge treatments can be categorized into plasma surface modification[225], plasma deposition,[226] and plasma polymerization.[227] The plasma surface modification merely exposes the Ti and Ti alloys to the plasma. During the treatment, the surfaces of Ti and Ti alloys are impinged by ions and electrons, with aim to clean and sterilize their surfaces. This method can remove the native layer, thick oxides, and impurities on the surface of Ti and Ti alloys by argon (Ar) plasma. Afterward, Ti and Ti alloys can be reoxidized in pure O_2 atmosphere to reduce carbon contamination in the native oxides.[224,228] Meanwhile, plasma surface modification also increases the surface energy and wettability of Ti and Ti alloys.[228] However, during plasma surface-modification treatment, contaminations may also take place via the deposition of materials from the plasma container (e.g., Fe and Si) or inappropriate processing parameters.[224] In contrast, the plasma deposition uses glow discharge to synthesize a coating from solid targets or plasma gas.[226] Therefore, the surface compositions of Ti and Ti alloys are significantly changed depending on the plasma used. For example, nearly stoichiometric oxides could be generated in O_2 plasma. The final thickness of the layer produced by plasma deposition depends on the treatment parameters of gas pressure, time, and current density.[224,229] Similar to oxidation, nitride, oxynitride, carbide, and carbonitride layers can also be produced by corresponding plasma gas.[229–232] Apparently, chemical reactions may take place during plasma deposition. However, plasma deposition technique is classified as a physical method since the chemical reaction is not the primary mechanism during deposition. Plasma polymerization is a popular technique which can enable better immobilization of bioactive molecules on a "bioinert" Ti metal as polymeric substrates have demonstrated a considerable number of reactive functional groups.[233] Among the plasma polymerization techniques, the ammonia plasma treatment is frequently used, which modifies the Ti surfaces by polymerization of oxygen- and nitrogen-containing volatile chemicals such as methyl alcohol and amine.[234] Such chemicals are introduced to a quartz reaction chamber and the plasma is applied by a radiofrequency (RF) generator. This equipment is coupled with a plasma reactor and the Ti substrates are placed in the plasma reactor downstream from the plasma gas inlet. Such a treatment is conducted at about 10–50 Pa for from several seconds to dozens of minutes.[227,233,234] After removing the unreacted species, the plasma polymerization treatment is completed. The surface density of amino groups depends on the time of treatment.

Due to their wide applications, glow discharge plasma techniques are animated from the past to the present in the surface modification of Ti and Ti alloys. Aronsson et al.[224] used direct current glow discharge plasma treatment to clean and modify Ti implant surfaces; the surface contaminations and native oxides can be easily removed by Ar plasma associated with appropriate parameters used. In the meantime, oxidation and nitridation in O_2 and N_2 plasmas can obtain a controllable thickness of layers by varying the processing parameters. Ou et al.[235] synthesized an amorphous-like Ti oxide layer on Ti–6Al–4V substrate by Ar/O_2 plasma and the treated Ti–6Al–4V showed a significant improvement in human osteosarcoma cells (MG63) culturing compared with the untreated counterpart (**Figure 2**). Rossi et al.[231] reported that the glow discharge nitrided Ti–6Al–4V alloy shows a higher corrosion resistance in NaCl, HCl, and Na_2SO_4 compared with untreated Ti–6Al–4V. Borgioli et al.[236] compared the hardening effects of CP–Ti by furnace treatment and glow discharge treatment and they pointed out that glow discharge treatment is more efficient in hardening the surface of CP–Ti compared with the furnace treatment. Such useful properties of Ti and Ti alloys (in terms of corrosion resistance, wear resistance, and biocompatibility) were also enhanced by plasma-produced nitrided, oxynitrided, and carbonitrided diffusion layers.[237–239] The plasma polymerization technique is generally used to produce an active surface on Ti and Ti alloy substrates for better immobilization of bioactive molecules. This method can introduce both primary and secondary amino groups on the Ti substrate, which can enhance the bioconjugation reactions.[240] Puleo et al.[233] used the ammonia plasma treatment on Ti–6Al–4V surface and found that the activated Ti–6Al–4V surface induces significant osteoblastic activity in mouse pluripotent fibroblastic cells (C3H10T1/2). Akhavan et al.[241–243] used ion-assisted plasma polymerization to activate CP–Ti sheets and fabricated Ag nanoparticle-functionalized surface based on wet-chemistry methods. Their results indicate that most samples show above 70% killing efficiency against *Staphylococcus aureus* and promote the adhesion and proliferation of mammalian cells. Finke et al.[244,245] prepared amino-functionalized surfaces by plasma polymerization and such surfaces show enhanced adhesion and spreading of MG63 cells. Similar results can also be found in other studies.[246–249] As mentioned earlier, most work with respect to glow discharge plasma treatment for Ti alloys has primarily focused on the biomedical applications.

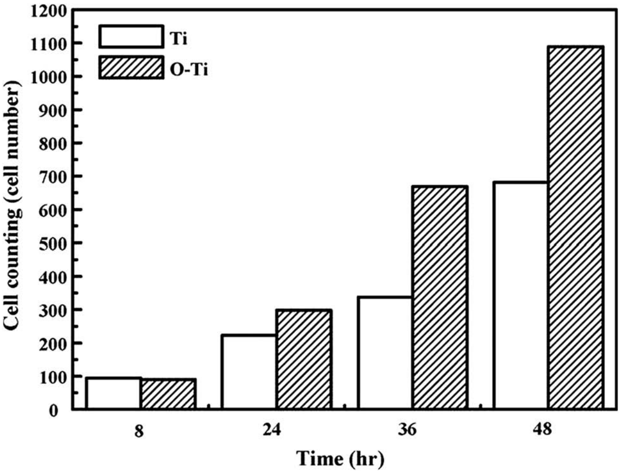

Figure 2. Cell numbers on glow discharge plasma treated Ti–6Al–4V and untreated counterpart after culturing human osteoblast-like cells (MG63) for different time. (Reproduced with permission.[235] Copyright 2008, Elsevier).

2.3. Chemical Methods

In comparison with physical methods, chemical reactions take place at the interface of Ti products and the imposed media (solution or gas phase) in chemical methods. Surface-modified layers formed on the surfaces of Ti alloys are produced based on redox reactions. Conventional chemical methods principally involve chemical treatments and electrochemical treatments.

2.3.1. Chemical Treatments

Chemical treatments basically include pickling, alkali treatment, passivation treatment, and hydrogen peroxide treatment. Pickling aims to remove the native oxides/contamination and to obtain a clean surface of Ti and Ti alloys.[250,251] Usually, hydrofluoric acid,[250,251] sulfuric acid,[252] hydrochloric acid,[253] and mixed acid solutions[167,254–256] (such as sulfuric acid/hydrochloric acid, hydrofluoric acid/nitric acid) are used as pickling solutions. The main effect of pickling is attributed to the decomposition of TiO_2 by the attack of H^+ in the solutions, which can also react with Ti to form soluble Ti compounds (or complexes) and hydrogen. However, the absorption of free hydrogen can lead to the hydrogen embrittlement in the surface layer of Ti and Ti alloys. Therefore, the concentration of acid solution is generally controlled at a low level.[1] The surface topographies of acid-treated surfaces of Ti and Ti alloys depend on the treatment conditions (e.g., temperature, concentration of acid solution, treatment time, and agitation). After the acid treatment, significantly thin (below 10 nm) oxide layers can be formed on the surfaces of Ti and Ti alloys as well as specific surface topographies associated with chemical composition modification. The oxide layers has an extremely low growth rate of 3–6 nm during a 400-day period.[257] The specific surface topographies may render a fast growth of bone cells. Lamolle at el.[250] found that the hydrofluoric acid treated CP–Ti disk shows a higher roughness and it demonstrates almost two times of mouse embryonic osteoblastic precursor cell (MC3T3-E1) attachment compared with the untreated counterpart. Similar results were also reported by Guo et al.[251] in both in vitro and in vivo tests for CP–Ti. Although pickling can enhance some properties of Ti and Ti alloys, such a treatment is often jointly used with other treatments, for instance blasting[251] or alkali treatment, to further improve the performance of Ti alloys.[258,259]

Alkali treatment soaks Ti and Ti alloys in high concentrated (4–10 M) NaOH or KOH solutions for several hours to produce surface-modified layers composed of sodium titanate gel.[260,261] Alkali treatment is often followed by heat treatment around 600–800 °C.[261] Afterward, a porous and bioactive surface can be formed on the treated Ti and Ti alloys. The detailed reactions during alkali treatment and heat treatment proceed simultaneously with the hydration of Ti as follows

$$\mathrm{Ti} + 3\mathrm{OH}^- \rightarrow \mathrm{Ti(OH)}_3^+ + 4\mathrm{e}^- \tag{1}$$

$$\mathrm{Ti(OH)}_3^+ + \mathrm{e}^- \rightarrow \mathrm{TiO}_2 \cdot \mathrm{H}_2\mathrm{O} + \frac{1}{2}\mathrm{H}_2 \tag{2}$$

$$\mathrm{TiO}_2 \cdot \mathrm{H}_2\mathrm{O} + \mathrm{OH}^- \rightarrow \mathrm{HTiO}_3^- \cdot n\mathrm{H}_2\mathrm{O} \tag{3}$$

Incorporation of $\mathrm{HTiO}_3^- \cdot n\mathrm{H}_2\mathrm{O}$ and the alkali ions can generate a hydrogel layer containing alkalinic titanate. The subsequent heat treatment leads to the dehydration and densification of hydrogel layer. As a result, the chemical compositions and surface topographies of Ti and Ti alloys are modified, which results in a porous surface layer consisted of rutile and anatase phases. **Figure 3** compares the scanning electron microscopy (SEM) microstructure of the polished and alkali-treated surfaces of CP–Ti.[262] It is found that the alkali-treated CP–Ti has a fine porous surface. Such a layer has been demonstrated to possess good bioactivity. Kim et al.[260] soaked CP–Ti, Ti–6Al–4V, Ti–6Al–2Nb–Ta, and Ti–15Mo–5Zr–3Al in 10 M NaOH or 10 M KOH solutions and followed by heat-treated at 600 °C for 1–24 h; they pointed out that the resultant surface gradually changes from the outermost apatite layer to the inner Ti. Nishiguchi et al.[262] found that alkali- and heat-treated CP–Ti can bond to bone directly, but only alkali-treated counterpart could not firmly bond to bone, illustrating the necessity of heat treatment for the alkali-treated CP–Ti in orthopedic applications. Indeed, the good bioactivity of the alkali- and heat-treated Ti alloys should be attributed to the formation of biologically active bone-like apatite layers on their surfaces in simulated body fluid (SBF).[263,264] Jonášová et al.[263,264] found that NaOH treated CP–Ti displays increased degree of supersaturation of SBF by releasing Na^+, leading to the formation of HA covered on the surface of the sample. However, the excessive release of Na^+ may cause an inflammatory response in the human body, which can lead to cell death.[263] Therefore, the NaOH-treated samples are generally washed by distilled water to control the content of Na^+ on their surfaces. It was also reported that the construction of bone-like apatite layers depends on the soaking solutions used.[265,266] Kim et al.[265] soaked alkali-treated CP–Ti in an amorphous calcium phosphate solution to prepare calcium phosphate layer. Similar scenario was also reported by Zheng et al.,[266] who used the same soaking solution to alkali-treat a β-type Ti–Nb–Zr–Sn alloy. It should be noted that pickling is generally conducted before alkaline treatment to clean the surfaces of Ti and Ti alloys. The advantage of the alkaline treatment for Ti and Ti alloys in biomedical applications is ascribed to the formation of biologically active bone-like apatite layers in SBF compared with the characteristics of pickling.

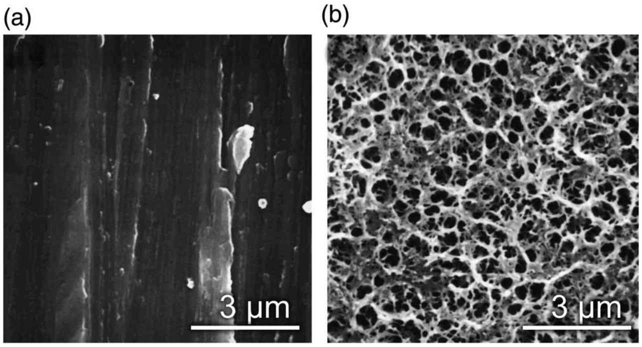

Figure 3. SEM images for the a) polished and b) alkali-treated surfaces of CP–Ti. (Reproduced with permission.[262] Copyright 1999, Elsevier).

Another chemical treatment method is passivation treatment, which is used to obtain uniform passivation films on the surfaces of Ti and Ti alloys. The passivation films can improve the corrosion resistance of Ti products, thereby decreasing their loss in the corrosive environments. Primarily, passivation treatment can be divided into two main groups: 1) acid passivation, i.e., soaking in strongly oxidizing acid solutions (such as high concentrated nitric acid[267,268] or phosphoric acid[269,270]); 2) thermal oxidation, specifically, heating in an O_2-containing atmosphere[157,268,271] or soaking in boiling water.[157,272] Unlike pickling treatment, soaking in the oxidizing acid solutions to obtain a passivation state can preserve the overall surface topographies of Ti and Ti alloys to a large extent due to the neglected dissolution. Many work revealed that the passivation treatment can produce thin oxide layers (2–6 nm) on Ti and Ti alloys and the phase constituents of these layers mainly consist of TiO_2 and trace other oxides (depending on the chemical compositions of alloys).[257,268] A gradient zone (suboxide layer) between the oxide layer and the Ti substrate was also reported, which has a thickness of several tens of nanometers.[273] Due to their considerably small thickness, the oxide layers formed on Ti and Ti alloys by passivation treatment are rather difficult to be exactly examined by microstructural characterization methods (e.g., SEM). An abnormal phenomenon is that nitric-acid passivation treatment enhances the ion release from Ti–6Al–4V alloy than that from the untreated Ti–6Al–4V.[274,275] However, this phenomenon was not observed in CP–Ti.[273] It is speculated that micro-galvanic effect would spontaneously take place between different phases in dual-phase Ti–6Al–4V, which facilitates to form a heterogeneous oxide layer, thereby resulting in release of trace element.[64,275] Phosphoric acid is another commonly used acid solution to conduct the passivation treatment.[269,270,276]

The characteristics of phosphoric acid passivation treatment increase the surface roughness, resulting in the formation of a $Ti_2O(PO_4)_2(H_2O)_2$ layer on the surface of CP–Ti.[269] The phosphoric acid treated sample with such a layer shows a better bioactivity to osteoblast cells compared with the purely mechanical treated sample.[269] In addition to acid treatment passivation, heating in an O_2-containing atmosphere or soaking in boiling distilled water have been used as alternative passivation treatments for Ti and Ti alloys. Such treatments hardly influence the surface topographies of Ti and Ti alloys but produce an oxide film (mainly TiO_2) with thickness of around 30 nm.[277] In comparison to the passivation by nitric acid, Ti–6Al–4V alloy passivated by boiling water shows a reduced ions release compared with the untreated counterpart.[157,271] Bloyce et al.[158] conducted thermal oxidation on CP–Ti, Ti–0.05Pd, and Ti–6Al–4V and found that the treated materials demonstrate simultaneously improved corrosion resistance and wear resistance. The predominant reason accounting for these improvements is the protective ability and limited plastic deformation of TiO_2 layer.[158] As such, passivation treatments can render Ti and Ti alloys to be used in multiple applications.

Inflammatory reactions are often found after implantation of Ti and Ti alloys, leading to the production of hydrogen peroxide.[278,279] Hydrogen peroxide can further react with Ti and Ti alloys to produce amorphous titania gels that are considered as an important role in the subsequent forming apatite on the surface of Ti implants.[280,281] Therefore, hydrogen peroxide treatment is used for the chemical dissolution and oxidation of Ti implant surfaces as well as the pretreatment for apatite formation.[282–284] The features of hydrogen peroxide treated surface, including the roughness and the thickness of titania gel layer, strongly depend on the hydrogen peroxide concentration and treatment time.[285] The titania gel layer can be transformed from the amorphous to crystalline by heat treatment. It has been reported that the heat treatment ranging from 300–600 °C can primarily transform titania to anatase in the gel layer.[285] However, raising the temperature of heat treatment would increase the content of rutile in the titania gel layer and degrade the bioactivity.[285] In general, the heat-treated sample enables the deposition of apatite after immersion in SBF for a short period.[286] The amount of apatite depends on the thickness of the titania gel layer. As such, the hydrogen peroxide treatment becomes a widely used method for Ti and Ti alloys in orthopedic applications.[282,284,287]

2.3.2. Electrochemical Treatments

Similar to chemical treatments, electrochemical treatments were also developed based on the chemical reactions occurring on the surface of Ti and Ti alloys. In such methods, electrical power source is necessary. The processed sample is designed as one of the electrodes. Hence, chemical reactions are controlled by the electrolyte and the processing parameters such as potential, current, and temperature. Basically, electrochemical treatments involve electropolishing, anodic oxidation, electrodeposition, and electroplating.

Electropolishing is a very commonly used method to obtain an expected surface finish of metallic materials.[288,289] When electrical power is exerted, a controllable electrochemical dissolution takes place on the surface of the anode (processed metal) at the given conditions of electrolyte, potential, current, and temperature. The viscous layer is significantly thin at the protruding parts of anode surface, which has a higher electropolishing current. Therefore, the protruding part has a faster dissolution rate than the sunken parts, resulting in a homogeneous and smooth finish surface.[290] For Ti and Ti alloys, the electrolyte usually consists of a mixture of acid and alcohol, such as perchloric acid/butanol/methanol.[290,291] Depending on the processing parameters, the removal rate of Ti and Ti alloys (dimensional change) is in the range of 1–10 $\mu m\ min^{-1}$. Because of the nonmechanical removal of Ti and Ti alloys, a crystalline termination under the oxide layer is introduced after electropolishing and the roughness of surface becomes very small ($R_a < 10$ nm). Thanks to these promising characteristics, electropolishing can produce a reproducible and well-defined commencement for subsequent other surface treatments. Larsson et al.[291] found that the electropolished CP–Ti sample displays a relative lower surface roughness (R_{rms}: 2.9 ± 2.9 nm) and therefore exhibits a significantly lower bone growth in animal test compared with the commonly machined counterpart (R_{rms}: 30.3 ± 19.8 nm). However, the anodic oxidation of electropolished CP–Ti sample leads to a high surface roughness (R_{rms}: 116.7 ± 40.2 nm) and a thicker oxide film. The commonly machined CP–Ti sample still has relatively low surface roughness (R_{rms}: 40.8 ± 14.7 nm). Therefore, the electropolished CP–Ti sample has a higher rate of bone growth than the commonly machined counterpart after anodic oxidation. Such findings indicate that surface topography influences the bone response to Ti and electropolished surface may be a better pretreatment for other surface-modification methods in biomedical applications. However, rare literature has reported the enhancements in hardness and wear resistance of Ti and Ti alloys by electropolishing.

Anodic oxidation is a well-acknowledged method for preparing different oxide films on metallic materials.[292] In this process, metallic material is used as anode. In comparison to passivation, anodic oxidation reactions are driven by electric field which can promote the diffusion of metal ions and oxygen ions, resulting in the formation of oxide film on the surface of anode.[293–296] For Ti and Ti alloys, several electrolytes, such as sulfuric acid, phosphoric acid, acetic acid, chromic acid and others, have been used for electrolytic solutions in anodic oxidation. The main advantage of anodic oxide films on Ti alloys is the enhanced adhesion and wear resistance, which mainly aims to serve the electronics and aerospace industries.[16,185,297] Fortunately, the formed oxide films on Ti and Ti alloys also have the functions of improving corrosion resistance and decreasing ions release.[298] Therefore, anodic oxidation can also be used for biomedicine. The structures and properties of anodic oxides can be controlled by altering the processing parameters, including potential, current, electrolyte, and temperature.[16,297,298] During anodic oxidation, the main reactions are shown as follows.[1]

At the Ti/Ti oxide interface

$$Ti \leftrightarrow Ti^{2+} + 2e^- \tag{4}$$

At Ti oxide/electrolyte interface

$$2H_2O \leftrightarrow 2O^{2-} + 4H^+ \tag{5}$$

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad (6)$$

The overall reaction

$$Ti^{2+} + 2O^{2-} \leftrightarrow TiO_2 + 2e^- \quad (7)$$

Although the formed oxide film (mainly TiO_2) has a high resistivity to the electrical circuit consisting of the electrolyte and the metallic part, the oxide film would continuously grow as long as the electric field is strong enough to drive the ions through the oxide film. The final thickness of oxide film is approximately proportional to the applied potential. However, the formed oxide has a breakdown potential of about 100 V.[299] If anodic oxidation is conducted at a voltage above the breakdown limit, the oxide film would not be resistive enough. As a result, increased gas evolution and frequent sparking would take place during such an anodic process. Typically, a nonuniform and porous oxide film is formed in this situation. Such a process is also called as micro-arc oxidation (MAO) or plasma electrolytic oxidation,[299] which will be introduced in Section 3.3.1. Therefore, only anodic oxidation below the breakdown limit of oxide is discussed in detail in this section. Oxide films prepared on Ti and Ti alloys by anodic oxidation show complicated surface morphologies and microstructures.[299] The morphologies of oxide films are dependent on their thickness (usually increase in roughness associated with increasing the thickness) and the topographies of the underlying substrates. Similar memory effects were observed between the microstructures of oxide films and Ti substrates, which is attributed to the distinct growth rates of oxides on the different phases in metallic materials.[64,169] The anodic oxidation treated Ti and Ti alloys demonstrate a lot of improved properties compared with the untreated counterparts, with respect to both compositions and microstructures. For example, due to the compactness and rigidity of anodic oxide films, Ti and Ti alloys exhibit higher hardness, higher mechanical properties, enhanced corrosion resistance, and even better biocompatibility.[299–303] As shown in **Figure 4**, Leinenbach et al.[303] conducted anodic oxidation on CP–Ti in 1 M H_2SO_4 and found that the anodic oxidized CP–Ti can withstand higher stress amplitude (325 MPa) in the fatigue test compared with the air-oxidized CP–Ti (275 MPa). Yang et al.[300] reported that anatase and rutile phases are found in anodic oxide films, which induce the formation of apatite in SBF and benefit for the cell growth. For biomedical applications, calcium and phosphorus ions can be incorporated into anodic oxide films in an electrolytic solution containing dissolved calcium and phosphorus compounds.[298,304] TiO_2 nanotubes can also be synthesized on the surface of CP–Ti using 0.36 M NH_4F solution as electrolyte.[305] Meanwhile, anodic oxide films can be used as electrolyte membrane due to their acceptable insulant property.[185,306] Moreover, because of their improved adhesion and bonding, anodic oxide films were also used as base coating for subsequent electroplating or other coating technologies.[128,307] Another striking feature is that the vivid colors of oxide films are displayed by controlling their thickness as light can be interfered in films.[308,309] These advantages of anodic oxidation make Ti and Ti alloys be utilized in a variety of industries and the anodic oxidation technology is still currently being used in industry.

Electroplating and electrodeposition are two similar methods that can synthesize coatings on Ti and Ti alloys. Both methods should use electric power source and the processed metal is used as one of the electrodes. Electroplating uses electric current to reduce dissolved metal cations, then the reduced metal cations can form a coherent metal coating on the cathode.[128] Therefore, the plated coatings are commonly the simple metals. Electrodeposition synthesizes the coatings from aqueous solution, nonaqueous solution, or even fused salt under the effect of electric field and a series of electrochemical reactions, which can refer to a wide range of processes including cathodic electrodeposition, anodic electrodeposition, electrocoating, etc.[310] Generally speaking, electroplating can be regarded as one of electrodeposition methods. Ti is a significantly active metal so that an nonconductive oxide film always covers the Ti substrate, which undoubtedly impairs the bonding of the subsequent prepared metallic coating.[128] Hence, it is necessary to adopt pretreatment to remove this nonconductive oxide film before electroplating and/or electrodeposition.

Irrespective of the pretreatments, there are various applications for the electroplated Ti and Ti alloys in aerospace and electronics industries, depending on the properties of the plated

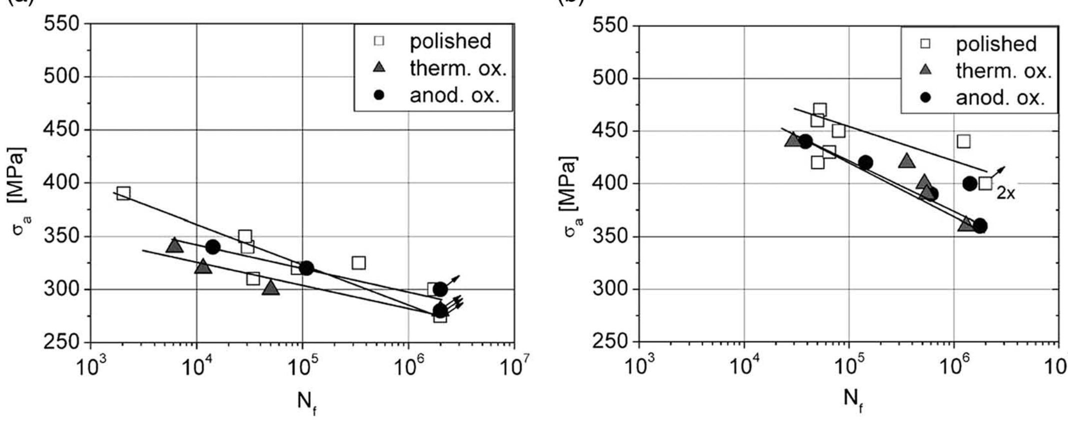

Figure 4. Effective stress (σ_a) versus number of cycles to failure (N_f) for polished, thermally oxidized (therm. ox.) and anodically oxidized (anod. ox.) CP-Ti: a) axial loading, b) rotating bending. (Reproduced with permission.[303] Copyright 2009, Elsevier).

simple metal films.[311,312] Similar to the electroplating, electrodeposition also can prepare simple metal films on Ti and Ti alloys with aim to enhance their hardness, wear resistance, or oxidation resistance.[313–315] Nevertheless, in comparison to the electroplating, both metallic and nonmetallic films can be coated on Ti and Ti alloys by electrodeposition.[316–318] Gilroy and Stevens[319] investigated the electrodeposition of PbO_2 on CP–Ti wires in a mixed solution of 0.5 M $Pb(NO_3)_2$ and 0.1 M HNO_3 for electrowinning applications. González-García et al.[320] also successfully prepared PbO_2 on a rough CP–Ti surface by electrodeposition. Jin et al.[321] electrodeposited Al_2O_3 coatings using 0.4 M $Al(NO_3)_3{\cdot}9H_2O$ ethanol solution and found that the coated CP–Ti shows enhanced oxidation resistance and corrosion resistance. Song et al.[322] prepared carbon films on CP–Ti plates and wires in molten LiCl–KCl–K_2CO_3 to improve their wear resistance. Because Ti and Ti alloys are prosperous as biomedical materials, electrodeposition technology is used for further improving the biocompatibility and bioactivity of Ti implants by synthesizing bioceramics on their surfaces. HA coatings,[305,323,324] calcium phosphate coatings,[325–327] composite coatings[328–330] have been synthesized by electrodeposition on Ti and Ti alloys, which can be the candidates for biomedical applications. Among these coatings, composite coatings may have a promising future in biomedical applications due to their multiple functions or better properties. Huang et al.[329] prepared HA/$CaSiO_3$ composite coating on CP–Ti and found that MC3T3-E1 cells have a high proliferation on the HA/$CaSiO_3$ composite-coated CP–Ti than the HA-coated CP–Ti. Gopi et al.[328] found that carbon nanotubes (CNTs) reinforced HA composite coating shows enhanced strength and toughness and improved biological properties compared with the sole HA coating. Due to their convenience and versatility, electrodeposition methods are still actively used in the current decade. Electrodeposition can synthesize a wide range of materials using various electrolytes on base metals with irregular shapes.[331] These are the main advantages of electrodeposition technology.

3. Advanced Surface-Modification Methods

Because of the prosperity of new processing technologies, a considerable number of advanced surface-modification methods have emerged in the recent years, such as friction stir processing (FSP), laser surface modification, and MAO. These methods offer new solutions to obtain better surface properties of Ti and Ti alloys. Basically, these newly emerged methods can also be classified into mechanical methods, physical methods, and chemical methods. Additionally, biochemical and drug-load technologies become useful surface-modification methods to improve the bioactivity and biofunctionality of Ti and Ti alloys for meeting the clinical requirements currently. The detailed information about these advanced surface-modification methods is presented as follows.

3.1. Advanced Mechanical Methods

It is well known that ultrafine-grained materials, which have the grain sizes in submicron or nanometer, often exhibit enhanced mechanical properties, corrosion resistance, and biocompatibility compared with their coarsening-grained counterparts.[12,332–340] Ultrafine-grained materials generally can be obtained by severe plastic deformation.[341–344] Therefore, some methods with respect to severe plastic deformation on the surface of Ti and Ti alloys are developed to obtain an ultrafine-grained surface-modified layer.[345,346] This section introduces two advanced mechanical methods involving FSP and surface mechanical attrition treatment (SMAT).

3.1.1. Friction Stir Processing

FSP is a surface-modification method derived from friction stir welding. Similar to friction stir welding, FSP uses a stir tool, consisting of a shoulder and a pin, to exert severe plastic deformation on the surface of the processed materials in a milling machine.[345] It should be noted that severe plastic deformation is induced by the friction between the stir tool and the surface of the material. When the stir tool commences the rotation, heat is generated as a result of friction and the materials become weak with increasing the temperature. Meanwhile, the stir tool moves along the predesigned route. As a result, an ultrafine-grained (down to nano-size) surface-modified layer is successfully obtained on the surfaces of the processed material under the combined effect of heat and deformation force as severe plastic deformation and dynamical recrystallization take place during FSP treatment.[347–353] Due to the relatively high hardness of Ti and Ti alloys, conventional stir tool has a significant consumption during processing, so that only tungsten–rhenium alloys can be used as stir tool.[345] The severe plastic deformed layer displays a gradient zone, which has a gradual increase in grain size from the most outer surface layer to the inner base alloy.[347] The width and depth of the severe plastic deformation surface layer is determined by the shape of stir tool. Furthermore, the processing parameters, including rotation speed and traverse speed, also have a great influence on the microstructures of the surface-modified layers.[350] Thanks to the refinement strengthening, surface-modified layers with ultrafine grains always exhibit higher hardness compared with the matrix. For ultrafine-grained materials, the sliding friction properties are always improved with increasing the hardness.[335,354,355] Hence, the wear resistance of the friction-stir possessed Ti and Ti alloys is apparently enhanced.[348,356] Meanwhile, the corrosion resistance of friction-stir processed Ti and Ti alloys is also improved under optimized processing parameters.[349] It is well known that the grains in submicron and nanometer have better bioactivity to osteoblast cells.[12] Therefore, the friction-stir processed Ti and Ti alloys can be used as candidates for biomedical applications as well as the other fields which have the requirements of wear resistance and corrosion resistance. Although FSP is used with the primary aim to obtain a surface-modified layer with refined microstructure, this process also can obtain composite layer by incorporating other functional particles in the prepunched holes, as shown in **Figure 5**a. For example, Yang et al.[165] filled Ag nanoparticles in prepunched holes before FSP and the amount of Ag was controlled by the depth of holes. Their results showed that the FSP-produced surface layers have promising antibacterial effects and both the *Staphylococcus aureus* (*S.a*) and *Escherichia coli* (*E.c*) decrease with increasing the Ag content after the

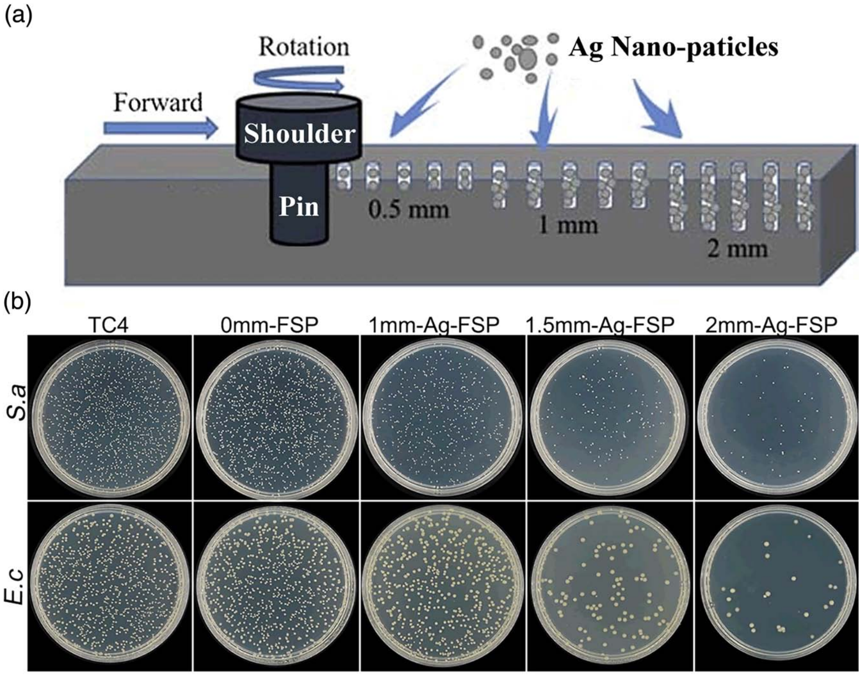

Figure 5. a) Schematic illustration of FSP for incorporating Ag nanoparticles (Reproduced with permission.[351] Copyright 2019, Elsevier) and b) typical *Staphylococcus aureus* (*S.a*) and *Escherichia coli* (*E.c*) colonies incubated on the samples after 24 h. The depth specifies the amout of Ag nanoparticles. (Reproduced with permission.[165] Copyright 2018, ACS Publications).

incubation for 24 h (Figure 5b). Similar results were also obtained by incorporating HA, TiO_2, Zn, TiC, and SiC nanoparticles for broad biomedical applications.[349,350,357,358] Combining the advantages of improvements in the hardness, corrosion resistance, wear resistance, and biofunctionality, FSP has a great potential in various applications. However, FSP has also apparent shortages. The low processing rate and the inferior flexibility usually limit the application of this technology to manufacture the workpieces with complicated shape and precise dimensional tolerance.

3.1.2. Surface Mechanical Attrition Treatment

SMAT is similar to SP, but SMAT was developed later than SP and also imposes impact on the workpieces repeatedly under a controlled atmosphere.[191,359] In comparison, SMAT uses hard steel balls in sizes of 3–10 mm in the velocities of 5–15 m s^{-1}.[360] It is well known that the equation for kinetic energy is $k = mv^2/2$ and the mass of ball (m) can be expressed as $4\rho\pi r^3/3$. Therefore, the kinetic energy can be written as $k = 2\pi\rho v^2 r^3/3 = Av^2 r^3$, where A can be considered as a constant for a specific type of balls used. As such, according to the data given in this work, it can be calculated that SP process has the kinetic energy of 0.0864–2812.5 A and the SMAT process has the kinetic energy of 84.375–28125 A. Hence, in a loosely speaking way, the hard steel balls in SMAT have higher kinetic energy than those in SP. SMAT induces severe plastic deformation in the surface layers of the processed materials and refined surface microstructures (even nanocrystallization) are hence obtained. Therefore, SMAT is frequently used to improve the surface properties of Ti and Ti alloys (and other metals as well) in the recent years.[194,346,361,362] As a similar method to SP, SMAT does have its own unique features. Due to its higher kinetics energy of impacting, nanocrystalline work-hardened surface layer formed via SMAT is thicker than that is formed via SP.[360] Correspondingly, SMAT can produce higher effective plastic strain and roughness in the surface-modified layer.[360,363] Zhu et al.[364] reported that a nanostructured layer in 50 μm thickness is produced on CP–Ti using stainless steel balls (in 3 mm diameter) treated for 16 min at a 20 kHz frequency. Jelliti et al.[365] also synthesized a 10 μm thick nanostructured layer on Ti–V. Similar to SP, the hardness, corrosion resistance, tensile strength, and wear resistance of Ti and Ti alloys are enhanced after SMAT due to the refined microstructure in the surface-modified layer.[365–368] Lai et al.[369] also reported that SMATed CP–Ti exhibits a better mesenchymal stem cells response compared with the untreated coarsen-grained CP–Ti. Interestingly, SMAT can combine with other surface-modification methods to obtain better properties for Ti and Ti alloys. It was found that the interactions between nanostructured Ti alloys and inflammatory-produced H_2O_2 are considerably limited.[370] Wen et al.[370] immersed SMATed CP–Ti into H_2O_2 solution for 24 h at 25 °C to prepare nanoporous titania on the surface, aiming to improve the biocompatibility. Yang et al.[371] used one-step chemical vapor deposition (CVD) to synthesize carbon nanofiber film on SMATed CP–Ti, which results in the dissolution of carbon atoms in the surface-modified layer through a considerable number of grain boundaries and other defects. Nitrided layers also can be produced on the SMATed CP–Ti and Ti–6Al–4V by plasma nitriding and gas nitriding.[363,372] Furthermore, Wen et al.[373]

found that the biomedical properties of CP–Ti are improved by combining SMAT and thermal oxidation. On one hand, SMAT reduces the grain size of CP–Ti to nanoscale, as the nanoscaled Ti grains have a better biological affinity with bone cells compared with coarse Ti grains. On the other hand, thermal oxidation would promote the formation of TiO_2 which also has better biological affinity than metallic Ti.[1] As shown in **Figure 6**, SMATed CP–Ti has a better osteoblast-like cell adhesion than coarse-grained CP–Ti.[373] Oxidized coarsening grained CP–Ti and oxidized SMATed CP–Ti are even better than SMATed CP–Ti.[373] In brief, SMAT treatment can be an effective solution to achieve some advantages of ultra-fine grained materials in a simple and economic way.

3.2. Advanced Physical Methods

3.2.1. Ion Implantation

Ion implantation technology can be classified into beam-line ion implantation and plasma immersion ion implantation.[374–377] The beam-line ion implantation uses a beam line (extracted from an ion resource) to directly bombard the surfaces of workpieces.[374] In the plasma immersion ion implantation, the materials are immersed in plasma and the ions bombard the surfaces of workpieces in a conformal manner via the plasma sheath.[374,378] Both methods should be processed in a vacuum to avoid the contamination of heterogeneous ions. In general, raster is used for beam-line ion implantation to accomplish the uniform implantation in a large area. Due to such a characteristic, beam-line ion implantation is still inconvenient to uniform implant ions in three dimensional (3D) workpieces with complex shapes.[374] In contrast, the workpiece is connected to a pulsed-biased negative potential in plasma immersion ion implantation and therefore ions can bombard the workpiece surface perpendicularly.[379] Hence, the workpieces with complex shapes might be successfully implanted. The substantial similarity between these two methods is that the implanted layers have the depths of 0.1–1 μm depending on the implantation dose and the ion energies.[379] According to different ion sources, distinctive layers, such as oxygen-ion implanted layer, nitrogen-ion implanted layer, carbon-ion implanted layer, metal-ion implanted layer, and so on, can be obtained on the surfaces of Ti and Ti alloys.

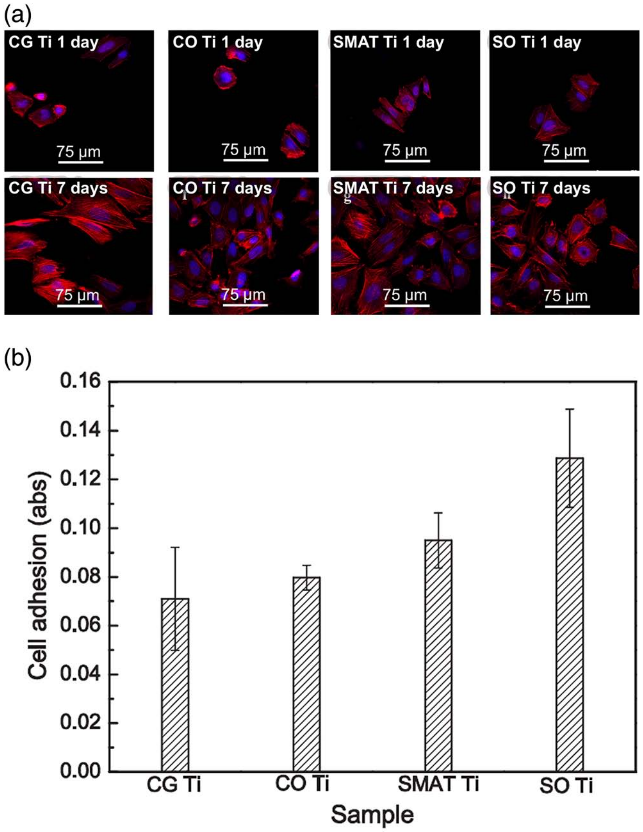

Figure 6. a) Morphologies of osteoblast-like cells on CP–Ti surface after 1-day and 7-day culturing and b) their adhesion after 7 days (the number of cells per surface). CG Ti and CO Ti indicate coarse-grained CP–Ti and oxidized coarsening grained CP–Ti, respectively. SMAT Ti and SO Ti represent SMATed CP–Ti and oxidized SMATed CP–Ti. (Reproduced with permission.[373] Copyright 2014, Elsevier).

Oxygen-ion implantation has been used for many metals to improve their mechanical and biological properties. Tan et al.[380] pointed out that the concentration of implanted ions decreases with increasing the implantation depth, and Ti–O and Ni–O compounds are formed in a plasma-implanted TiNi alloy. Li et al.[381] demonstrated that oxides would not form if the sample is processed at a low implantation dose. Therefore, the formation of compounds is closely related to the solid solubility of Ti and Ti alloys. All in all, many studies have reported that Ti and Ti alloys have the improved properties in wear resistance, corrosion resistance, and biocompatibility after oxygen-ion implantation. Mohan et al.[382] found that Ti–13Nb–13Zr has a simultaneous enhancement in both wear resistance and corrosion resistance after oxygen-ion implantation due to the formation of compact oxide film on its surface. As shown in **Figure 7**, oxygen-ion implanted Ti–13Nb–13Zr has an evident shallow scratch track compared with the untreated counterpart. Yang et al.[383] pointed out that the oxygen-ion implantation should be controlled at a proper dose to obtain the best biocompatibility; both vinculin and actin cells have the best growth on the oxygen-ion implanted CP–Ti at a dose of 4×10^{16} ions cm^{-2}. Tan et al.[380] indicated that oxygen-ion implanted TiNi exhibits the best corrosion resistance in Hank's solution at a dose of 1×10^{17} ions cm^{-2}. Like oxygen-ion implantation, nitrogen ion, carbon ion, and metal-ion implantations can also enhance the surface properties of Ti and Ti alloys. Nitrogen-ion implantation of Ti–6Al–4V shows the best wear resistance at a dose of 1×10^{17} ions cm^{-2}.[374] Carbon ion implantation can increase the hardness of Ti–6Al–4V by more than twofolds due to the formation of TiC precipitates or a TiC layer.[384] In the biomedical applications, both nitrogen ion implantation and carbon ion implantation show an improvement in the biocompatibility of Ti–6Al–4V.[385] Calcium and sodium ion implantation can enhance the formation of HA on the surface of Ti and Ti alloys due to the production of $CaTiO_3$ or $NaTiO_3$.[386–388] Silver-ion implanted Ti and Ti alloys possess antiinfective property and therefore they have been widely used as biomedical implants. Wan et al.[389] conducted the surface modification of

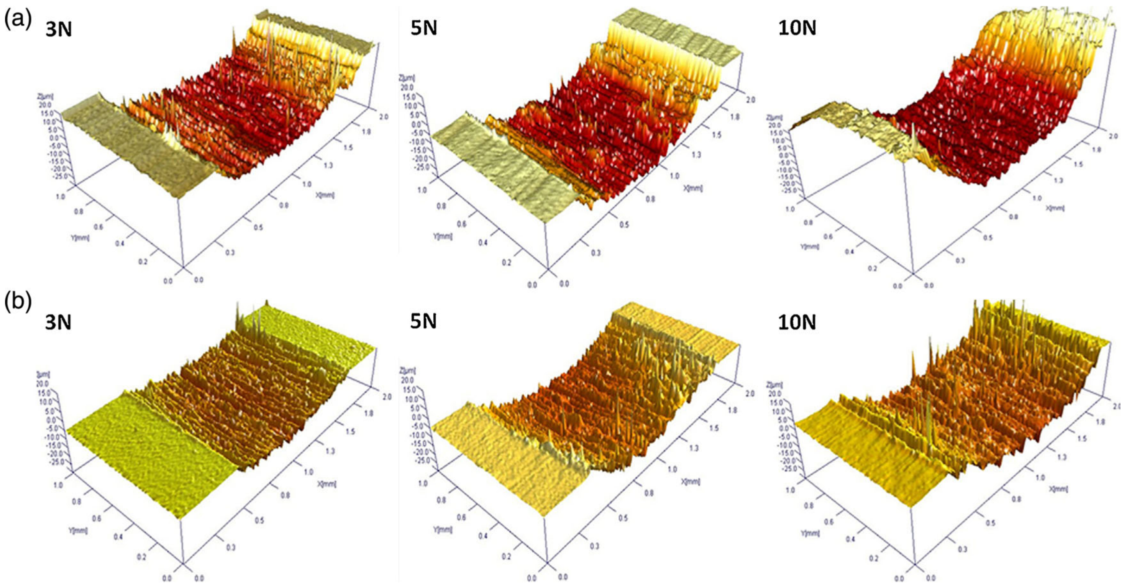

Figure 7. Profiles of the wear tracks at a load of 3, 5, and 10 N on a) untreated Ti–13Nb–13Zr and b) oxygen ion implanted Ti–13Nb–13Zr. (Reproduced with permission.[382] Copyright 2013, Elsevier).

CP–Ti and Ti–6Al–7Nb by ion implantation of Ag and Cu and found that both modified CP–Ti and Ti–6Al–7Nb show improved antibacterial activity and enhanced wear resistance. The increased antibacterial activity is ascribed to the antibacterial effect of Ag and Cu.[389,390] Jin et al.[391] investigated synergistic effects of dual Zn/Ag ion implantation in osteogenic activity and antibacterial ability of CP–Ti and pointed out that the coimplanted samples demonstrate the improved bioactivity and antibacterial function according to the in vitro and in vivo testing. This phenomenon is attributed to the combining effects of the long-range interactions rendered by Zn and short-range interactions of Ag in the Zn/Ag implanted CP–Ti. As such, ion implantation seems to substantially have the capacity to improve the various properties of Ti and Ti alloys. However, limitations of ion implantation are also apparent. Ion implantation is a capital-intensive method, leading to a restriction in its extensive use. Although plasma-immersion ion-implantation provides solution to the implantation of 3D workpieces, several preimplantation processing, such as masking and manipulator, must be prepared, which further increases the complexity and cost of this method.

3.2.2. Laser Surface Modification

Laser beam, which has high coherence and directionality, has been commonly used in the surface modification of many metals.[392–395] In laser-related surface-modification methods, a defocused laser beam is used as a heat source to melt materials on the surface of the processed workpieces. The melted materials may be the surfaces of the workpieces, the additional powder preplaced on the surfaces of the workpieces, or the synchronous feeding powder/wires. Therefore, laser surface-modification methods can be classified into laser surface remelting,[396,397] laser surface alloying,[398,399] and laser cladding.[400,401] Laser surface remelting uses an energic laser beam to melt the surfaces of workpieces. As such, a thin surface layer of the workpiece would be melted and solidify immediately. Such characteristics of laser surface remelting are also found in other laser processing technology.[402–405] For those metals with a HCP crystalline structure (such as Ti, Zr, and Mg), fast solidification rate would result in the formation of fine martensite structure, which stems from the transformation from BCC β phase to HCP α phase.[406–408] It was reported that fine martensite structure covered with a thin TiO_2 layer is formed on the surface of laser remelted Ti substrate.[392] Both fine martensite structure and TiO_2 layer have higher hardness and better wear resistance than the underlying substrate.[409] Meanwhile, due to the existence of compact TiO_2 layer formed on the surface, the corrosion resistance of the processed Ti and Ti alloys is also improved.[410,411] Laser surface remelting is an easy way to improve the wear resistance and corrosion resistance of Ti and Ti alloys. However, such an enhancement is also not necessary since the TiO_2 layer is significantly thin (typically less than 200 nm).[412]

Laser surface alloying can use both powder and gas as additives. During laser surface alloying, the additives react with the melt pool to produce an alloyed layer with the thickness of 0.5–1 mm.[392] Nitrogen is frequently used as the gas additive in laser surface alloying treatment. Because of the reaction between nitrogen and Ti, a TiN layer would be formed on the surface of Ti substrate. The thickness of TiN layer depends on the processing parameters, such as the energy density of laser and nitrogen flow. As represented in other surface-modification methods, TiN layer has a high hardness of 1000–1500 HV.[413–415] Therefore, TiN-coated Ti and Ti alloys possess significantly better wear resistance than their untreated counterparts.[413] Chan et al.[416] prepared nitrogen surface alloyed Ti–35.3Nb–7.3Zr–5.7Ta and found that the wear resistance and corrosion resistance are enhanced. Apart from laser gas surface alloying, using powder as additives can produce various alloying layers on the surfaces of Ti and Ti alloys. For example, Dutta Majumdar et al.[417] used Al and Si as additives for laser surface alloying on CP–Ti; they elucidated that Ti_5Si_3, Al_2O_3, and SiO_2 are formed on the surface layer, which effectively enhances the oxidation resistance of CP–Ti at 650/750 °C. Therefore, this method provides a solution to the application of Ti alloys used in aero-turbine engines. Sha et al.[418] obtained similar results by adding NiAl and ZrO_2. Tian et al.[419] added TiN–B–Si–Ni powder mixture to produce several intermetallic compounds, such as $Ti_6Ni_6Si_7$, TiB_2, NiB_2, NiTi, and TiNiSi, in the surface-modified layer of CP–Ti and found that its hardness, oxidation resistance, and wear resistance are significantly improved compared with the untreated substrate (**Figure 8**). Tian et al.[420] also used boron, graphite, Ce_2O_3, Y_2O_3, and pure Ti powder as additives to produce composite coatings on CP–Ti and Ti–6Al–4V; they pointed out that the addition of rare earth oxides (Ce_2O_3 and Y_2O_3) can refine the microstructure of the resultant coatings.

Another important laser surface treatment is laser cladding, which uses a defocused laser beam to melt the preplaced or synchronous feeding powder/wires, leading to form a coating on Ti and Ti alloys. Laser cladding exhibits the advantages of high homogeneity, high deposition rate, and low dilution of the substrate. In the selection of cladding materials, melting point, thermal expansion coefficient, and elastic modulus should be considered. Too much distinctions of such physical properties may lead to a low adhesion of coatings or a large residual stress in the coatings. Meanwhile, the cladding materials with low wettability to Ti substrate has difficulty in the formation of metallurgical bonding between the coatings and the Ti substrate.[393] Due to the high energy of laser, a variety of metals and ceramics have been used as the cladding materials. Simple metals are used as cladding materials for many years but rarely used in the recent years.[393] Therefore, simple metals would not be introduced in this section. For the other cladding materials, Meng et al.[421] used NiCoCrAlY to improve the hardness and wear resistance of Ti–6Al–4V; their results showed that the laser cladding produced NiCoCrAlY coating has a high hardness of 800–1000 HV, which is two times than that of the Ti–6Al–4V substrate. Mixed Zr–Cu–Al–Ni powder was cladded on CP–Ti substrates by Wang et al.[422] and a number of intermetallic compounds associated with amorphous phase were found in the resultant coating with high microhardness and low friction coefficient. Many intermetallic compounds, composite materials, such as Ti–Al,[423] Ti–Ni,[424] Ti–TiC,[425] Al–TiC,[426] and Ti–Ni–B_4C[427] have also been introduced in laser cladding, which can enhance the hardness, wear resistance, and oxidation resistance of Ti and Ti alloys. Cermets, which are also named as ceramics/metal composites, have received considerable attentions as cladding materials in the recent years due to their higher hardness and wear resistance compared with the simple metals or alloys.[428–433] TiN is frequently used as cladding material on Ti and Ti alloys. The prepared laser cladding coating shows two regions of remelted TiN and TiN/Ti mixed layer on the top and bottom.[429] Lin et al.[429] demonstrated that the wear loss of TiN cladding Ti–6Al–4V is only 1% that of its untreated counterparts. Selamat et al.[430] also successfully prepared laser cladding SiC coating on Ti–6Al–4V alloy and their result showed that the microstructure of the coating mainly consists of α′-Ti, $Ti_{0.55}C_{0.45}$, and Ti_5Si_3 phases. Molian and Hualun[431] used BN powder as cladding material to in situ synthesize a TiN + TiB_2 cermet coating on Ti–6Al–4V, and the coating showed high hardness of 1600 HV and superior wear resistance. However, using ceramics as cladding materials has an apparent shortcoming as the high hardness is always associated with the

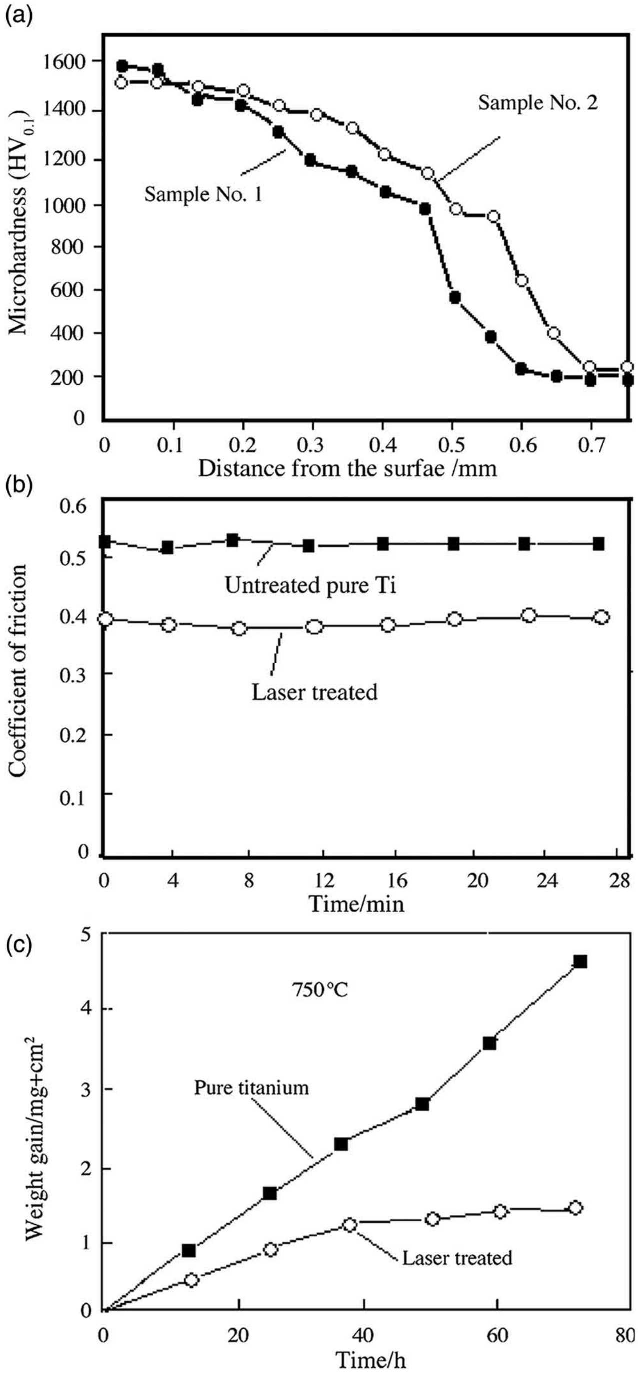

Figure 8. Laser surface alloying of CP-Ti with TiN–B–Si–Ni mixed powder: a) hardness profile of laser alloyed samples, b) friction coefficients versus time, and c) oxidation weight gain versus time for sample 2 and untreated CP-Ti. (Reproduced with permission.[419] Copyright 2005, Elsevier).

brittleness in ceramic materials. In the meantime, the reproduction is another major issue for laser cladding using ceramic materials. Laser cladding has also been used for Ti and Ti alloys for biomedical applications. Roy et al.[434] produced a tricalcium phosphate and Ti composite layer on CP–Ti by laser cladding, and the coating shows a simultaneous enhancement in hardness and bioactivity. Li et al.[435] prepared laser cladding $CaO–SiO_2$ coating on Ti–6Al–4V, and the coating is capable of forming calcium phosphate in SBF. The mechanism for the formation of calcium phosphate is shown in **Figure 9**.[435] The formation of silanol (REAL≡Si—OH) is induced by the exchange of calcium ions in the coating with H^+ in SBF solution. Hence, the functional group (REAL≡Si—O^-) forms on the surface of coating to produce a negatively charged surface, which provides the nucleation of apatite. Similar scenario was found using calcium carbonate, calcium hydrogen phosphate, Ti, and ceria powder mixture,[436] and the resulted coating has the ability to form HA and calcium phosphate in SBF.

As stated earlier, laser surface treatment can produce various surface-modified layers that can be applied in multiple service environments, such as aerospace applications and human body. However, there are still some problems with respect to these methods. Cracks are often found in the laser-cladding coatings, which is attributed to the residual stress produced during the remelting and solidification of the cladding materials and the surface of the substrate.[392] Hence, optimized processing parameters are always required. Low bond strength is also found in ceramics coatings (including bioceramics coatings) with substrates. Therefore, a buffer interlayer is often needed for laser surface treatment.[437]

3.2.3. Physical Vapor Deposition

During physical vapor deposition (PVD), single or multiple source materials are evaporated or sputtered in a high vacuum.[438,439] Subsequently, the formed atoms, molecules, or ions are transferred to the surface of substrate, leading to the nucleation and growth of a thin film.[438,440] Although PVD is classified as physical method, some reactions with the materials surface may still take place to facilitate the growth of film. The advantages of PVD-processed films have high density and strong adhesion to the substrate. Typically, PVD can be categorized into evaporation plating, ion plating, and sputtering.[1]

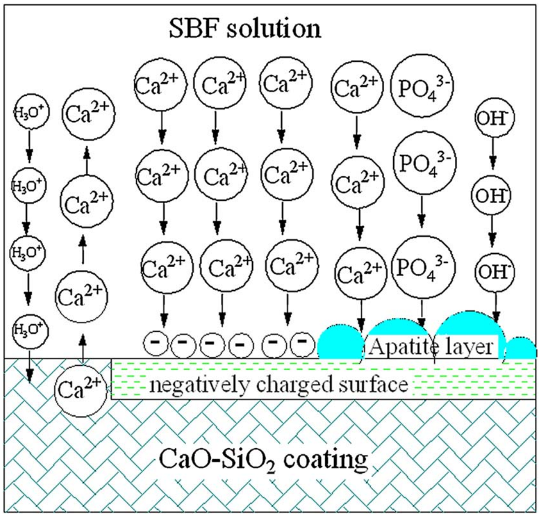

Figure 9. Diagram of the mechanism of apatite formation on laser cladding coating in SBF. (Reproduced with permission.[435] Copyright 2015, Elsevier).

A thermal-assisted phase transformation in source materials takes place during the evaporation plating. Generally, the deposition rate of evaporation plating is 10–25 000 nm min^{-1}.[1] Metals and compounds, including oxides, carbides, nitrides, and their mixtures can be used as source materials, which should be pure and free of gases and/or inclusions. Several source materials are often used to overcome their different evaporation rates (which results from distinctive vapor pressures) between different components in the source materials. The vaporized compounds are often difficult to fragment during deposition, which significantly declines the deposition rate. Therefore, using a metal evaporating in the reactive gas can deposit compound films on the substrate, resulting in the increase in the deposition rate and decrease in the deposition temperature. For example, TiC coating can be deposited by evaporating Ti in C_2H_2 or C_2H_4 flow.[441] TiN can be produced by evaporating Ti in N_2 flow.[442] Probst et al.[443] synthesized TiN and TiO_2 composite coating by evaporating Ti in mixed N_2 and O_2 gas flow. Such coatings show significantly higher hardness and enhanced wear resistance than the substrate and exhibit a better chemical and phase homogeneity compared with the counterparts prepared by other surface-modification methods (such as plasma nitriding).[442]

Ion plating is a process that uses energetic particles to bombard the substrate surface and deposit films. These high-energetic particles are the extracting ions from a confined plasma, compounds, alloy sputtering targets, or special ion sources.[1] Due to the bombardment of high-energetic particles, loosely-bound species (such as contaminants or nonreacted compound-forming species) can be removed during plating. Similar to evaporation plating, the deposition rate of ion plating is typically 10–25 000 nm min^{-1}.[1] Various films have been reported to be synthesized on Ti and Ti alloys, such as TiN, TiC, TiCN, TiAlN, TiSiN, diamond-like carbon (DLC), and hydrogenated amorphous carbon.[444–447] Ti and Ti alloys covered with such hard films always exhibit enhanced wear resistance and can be used in the cutting and forming operations. However, the huge difference in the hardness between films and Ti substrates often causes the potential delamination and cracks.[448] Therefore, Marin et al.[448] proposed to conduct a diffusive treatment at 800–900 °C to enhance the adhesion properties of the films. Yao et al.[449] deposited a TiSiN film on Ti–6Al–4V for marine applications and their results showed that the TiSiN film prepared at a negative bias voltage of 10 V has the best wear resistance in seawater. Furthermore, ion-plated films are also used in biomedical applications for Ti and Ti alloys. Vadiraj and Kamaraj[450] prepared a TiN-coated Ti–6Al–4V with a better fretting-fatigue resistance compared with uncoated counterpart, indicating that such a Ti alloy can be used as hip implants. Jones et al.[451] investigated the platelet attachment on ion-plated CP–Ti with TiN, TiC, and DLC films. The results showed that only a small degree of activation of platelets on DLC film is found on the surface, indicating a better hemocompatibility of TiN and TiC films compared with DLC film.

In comparison to evaporation plating and ion plating, sputtering has a lower deposition rate of 25–1000 nm min^{-1} as the deposited species should be ejected from a condensed-matter source by the impingement of energetic projectile particles.[452,453] However, some ceramics and refractory metals (i.e., having high melting points), which are difficult to deposit by evaporation plating, are prone to deposit by sputtering. Therefore, sputtering is a popular method that exhibits many advantages, including versatility and flexibility. In some cases, the sputtering technique is similar to the plasma-deposition technique. Both techniques may use plasma as working medium and somewhat overlap. However, solid target is generally used in the sputtering while solid target, and plasma gas can be used in the plasma deposition. Regardless of the relationship between the sputtering and plasma deposition, various sputtering methods, such as simple direct current sputtering,[454] RF sputtering,[455] ion beam sputtering (IBS),[456] magnetron sputtering,[454,457] and their combination have been reported to prepare thin film on Ti and Ti alloys to improve their wear resistance, corrosion resistance, biocompatibility, and bioactivity. Similar to other surface-modification methods, hard films such as TiN, TiC, and TiCN were used to improve the hardness and wear resistance of Ti and Ti alloys.[458–460] Li et al.[454] investigated the tribological properties of direct current magnetron-sputtered TiCuN with different additions of Cu. As shown in **Figure 10**a, the friction coefficients of the samples decrease with the increase in the addition of Cu. However, only the film with the addition of 1.44 wt% Cu shows a decrease in the wear rate compared with the substrate (Figure 10b). This finding illustrates that proper content of Cu in TiCuN film can flatten the wear tracks but not increase the roughness of the as-deposited film.[454] Therefore, one can conclude that the properties of the deposited films are significantly influenced by their chemical compositions. Similar work was conducted by Diserens et al.[461] by incorporation Si in PVD TiN films and their results showed that the hardness of prepared films increases with increasing the content of Si. For biomedical applications, Ewald et al.[462] developed a Ti/Ag film on CP–Ti and the film shows promising antimicrobial properties to *Staphylococcus epidermidis* and *Klebsiella pneumoniae*. The addition of Ag in the film shows a little negative effect on the osteoblast cells after a long-time culturing. To further improve the biocompatibility of Ti implants, Lindgren et al.[463] and Xia et al.[464] investigated the growth of HA films on a surface oxidized CP–Ti by PVD. Afterward, these surface-modified CP–Ti samples were immersed in the phosphate buffer solution for a week and the HA is formed on the surface of samples. The underlying mechanism is the same to the formation of apatite on the alkali-treated Ti alloys (please see Section 2.3.1). Cooley et al.[465] used HA as source material in the PVD processing and found that the obtained film is in an amorphous state. However, the PVD-prepared amorphous HA film is prone to dissolve in the service environment.[466] Therefore, a new biocompatible multilayered HA/Ti film on Ti–6Al–4V was developed.[467] Using RF magnetron-assisted sputtering to synthesize multilayered HA/Ti film can overcome its delamination after implantation in the human body.[468] Ding[468] pointed out that wide atomic intermixed zones are found in the near-interface region and coating/substrate interface region in the multi-layered HA/Ti film, which significantly contributes to the improvement of the adhesion strength.

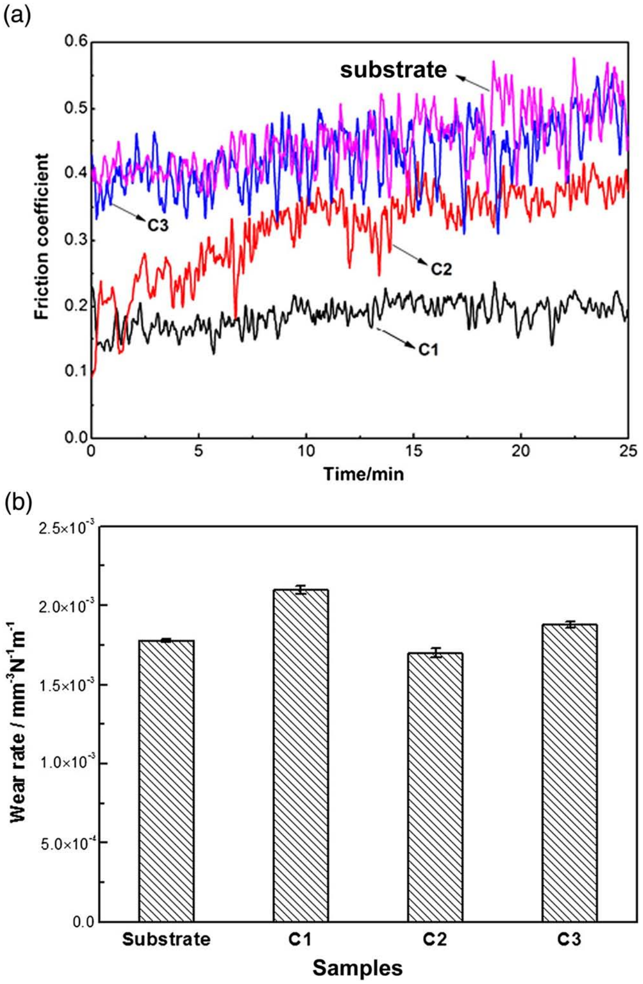

Figure 10. Tribological properties of direct current magnetron-sputtered TiCuN films and Ti–6Al–4V substrate: a) friction coefficient and b) wear rate. C1, C2, and C3 indicate the TiN films respectively prepared by the targets with the Cu/Ti ratio of 0.16%, 1.44%, and 4% (in wt%). (Reproduced with permission.[454] Copyright 2016, Elsevier).

3.3. Advanced Chemical Methods

3.3.1. Micro-Arc Oxidation

As mentioned earlier in Section 2.3.2, MAO can be regarded as a developed method from anodic oxidation, which is also named anodic spark oxidation or plasma electrolytic oxidation.[469–473] This method can synthesize ceramic coatings on the surface of many metals, such as Ti, Al, Zr, Mg, and other metals.[469,471,474] During the MAO process, the sample is used as anode and immersed in the an aqueous solution associated with a relatively high voltage. This voltage must be above the breakdown limit of the formed oxides. Hence, sparking, which leads to less uniform and more porous oxide films, frequently takes place on the surface of the processed samples. For TiO_2, the breakdown limit is about 100 V.[299] Therefore, the voltage of MAO is often conducted above 150 V for Ti and Ti alloys. After MAO treatment, porous coatings with high hardness, wear resistance, and adhesion could be produced. Such porous coatings improve the biocompatibility of Ti and Ti alloys.[155] Hence, MAO method is primarily used for Ti and Ti alloys in the biomedical applications.

The chemical compositions, morphologies, and microstructures of MAO-produced coatings strongly depend on the MAO parameters, such as alloy compositions, electrolyte, temperature, time, voltage, duty cycle (the ratio of the on-time to the total working time), current density, and so on. For example, the surface morphologies of samples are significantly influenced by the applied voltages as shown in **Figure 11**.[475] The biocompatibility examinations show that MG63 has a highest proliferation rate on the sample treated at 190 V and human osteosarcoma cells (e.g., MG-63) exhibit a best alkaline phosphatase activity on the sample treated at 600 V.[475] Such findings illustrate that the parameters used during MAO should take the service environments into consideration. Similar to voltage, current density has a significant influence on the microstructures and properties of the MAO coatings. Constant-voltage mode results in a freely decreased current density during MAO, which finally leads to a relatively smooth surface with low porosity. Shin et al.[476] conducted MAO on CP–Ti in a phosphate electrolyte for 300 s at different current densities of 100, 150, 200, and 250 $mA\,cm^{-2}$ and their results showed that the pore size decreases with decreasing the current density. Such a morphology facilitates the formation of apatite and the proliferation of osteoblast cells.[476,477] Higher duty cycle results in a higher on-time of electricity during each cycle, leading to a higher energy of spark.[478] Although there is no systematic investigation on the microstructure and properties of MAO-treated Ti and Ti alloys with respect to duty cycle, some studies on other metals show that increase in duty cycle can slightly decrease the coatings thickness but increase their porosity.[479] Apart from these

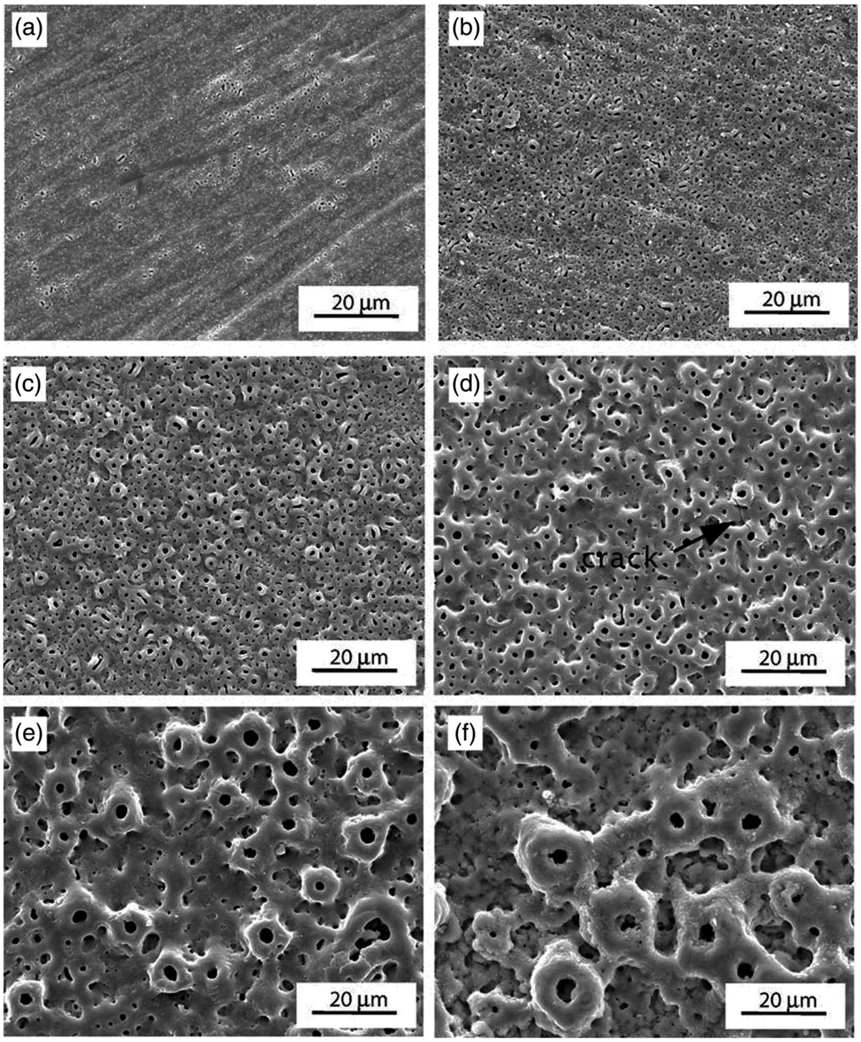

Figure 11. Surface morphologies of CP–Ti after MAO at different voltages: a) 190 V, b) 230 V, c) 270 V, d) 350 V, e) 450 V, and f) 600 V. (Reproduced with permission.[475] Copyright 2004, Elsevier).

processing parameters, the choice of electrolyte is extremely important to MAO coatings as the concentration and composition of the electrolytes influence the metal passivation, therefore the morphologies, thicknesses, and properties of the MAO coatings. In general, NaOH/KOH is used as the base electrolyte.[155] The electrophoresis can be used as an auxiliary method for MAO. Nie et al.[480] carried out MAO treatment on a Ti–6Al–4V alloy using a phosphate salt solution as electrolyte and followed by conducting electrophoresis using an HA powder aqueous suspension as electrolyte. Their results showed that a relatively thick TiO_2 film is produced by MAO and an HA coating formed on the TiO_2 film; the as-produced coating shows a porous appearance and better corrosion resistance in a buffered physiological solution compared with the untreated Ti sample. Some additives, such as phosphate, fluoride, silicate, sodium salt, and calcium salt, are frequently used as the primary additives in the base electrolyte.[481] Fluoride-containing electrolyte induces the formation of fluoridated HA in the MAO coatings, leading to a favorable bone response and interface adhesion.[481,482] Wang et al.[483] prepared Si-incorporated MAO coating on CP–Ti using simple electrolyte composed of NaOH and $NaSiO_3$; the Si-incorporated MAO coating shows better adhesion and proliferation of rat bone mesenchymal stem cells compared with the Si-free counterpart. Some other ions, such as strontium, manganese and copper, have been also considered to be incorporated in the electrolytes to improve the bioactivity or antimicrobial property of implant materials.[484–486] Ionic substitutions easily take place in apatite structure, hence multiple elements can be considered to modify the electrolyte, which may result in better biocompatibility and closer composition of the MAO coatings to human bone.[487] As a very popular method for surface modifications, MAO has a promising future in the biomedical applications for Ti and Ti alloys. As the produced TiO_2 in the micro-arc oxide film has good dielectric properties and photocatalytic performances, MAO technology is also used in electronics and environment protection industries.[481,488] However, there are still some questions needed to be solved. Low processing rate and high energy cost would limit the MAO technology in manufacturing industry as the cost of MAO is still high. Meanwhile, although MAO can also conduct on the workpieces with complex shapes,[489,490] the thickness of the MAO layer is not homogeneous due to the limitation of geometry. Yan et al.[489] conducted MAO on the porous Ti alloys and found that the MAO coating formed on the outer pore walls has a larger thickness and larger pore size compared with the MAO coating formed on the inner pore walls. Such a difference also causes the different compositions.[489] Although rare literature has mentioned the distinct properties in the different locations of porous Ti alloys, different thickness values may provide an evidence to specify their different properties. Furthermore, there is a lack of investigations on the design of electrolyte as well as the influence of substrate on the compositions of micro-arc oxide film. Therefore, the detailed mechanism for MAO is not well understood. These questions draw forth the future development of MAO technology. First, increasing the utilization of energy by optimizing MAO facility should be significantly considered, which can decrease the MAO cost to a large extent. Second, to complete the discharge model and film growth model of MAO is necessary in the further development of this technology. Third, combining some other methods (such as heat treatment and electrophoresis) to further enhance the performance of Ti and Ti alloys may be a trend for MAO technology targeting broad applications.

3.3.2. Sol–Gel

To introduce this method, the definition of colloid should be understood first. In general, a suspension with the dispersed fine particles (1–100 nm) is defined as a colloid.[491] Due to their small size, the gravity of the fine particles can be neglected and the interactions between them are controlled by van der Waals attraction and surface charges. A sol is a colloidal suspension with dispersed solid particles in the liquid and the solid particles connect each other to form a skeleton enclosing the liquid phase, namely, a gel.[492] The prepared sol–gel can be transferred to the surface of Ti and Ti alloys by different techniques, including spin coating, dip coating, spraying, and electrophoresis.[492–494] As such, several steps are presented in the sol–gel process.[495] First, a precursor solution is needed. Metal alkoxides ($M(OR)_n$) are the most frequently used as metalorganic precursors, where M indicates a metal or metalloid atom and R means an alkyl group. Metal alkoxides are normally dissolved in alcohol and hydrolyzed by adding water. Therefore, hydrolysis reaction takes place as the following reaction[1]:

$$M(OR)_4 + H_2O \rightarrow HO{-}M(OR)_3 + ROH \tag{8}$$

In the meantime, a condensation reaction takes place between two $HO{-}M{-}(OR)_3$ molecules[1]:

$$(OR)_3M{-}OH + HO{-}M(OR)_3 \rightarrow (OR)_3M{-}O{-}M(OR)_3 + H_2O \tag{9}$$

Furthermore, one hydrolyzed molecule can also directly react with one alkoxide molecule[1]:

$$(OR)_3M{-}OR + HO{-}M(OR)_3 \rightarrow (OR)_3M{-}O{-}M(OR)_3 + ROH \tag{10}$$

In such a case, a sol (colloid suspension) is formed by the interconnection of $(OR)_3M{-}O{-}M(OR)_3$. As the time elapses, the colloid suspension becomes a 3D network. If a molecule is big enough in size to extend the whole solution, such a solution is a gel. After gelation, the gel is transferred to the surface of Ti and Ti alloys by the techniques mentioned earlier. Afterward, syneresis turns the gel into an aerogel during aging and further drying turns the aerogel into an xerogel.[496] Even after drying, most gels may be in an amorphous state.[496] To produce a pore-free dense film with high degree of crystallinity, heat treatment at high temperature is required.[495] The advantage of sol–gel method is high homogeneity, which can be attained in the prepared films as the precursors can be mixed at a molecular level in the solution. Generally, the synthesized films are very thin ($<10\ \mu m$).

Various films, such as TiO_2,[497,498] SiO_2,[499] calcium phosphate, and composite films, have been synthesized on Ti and Ti alloys mainly for biomedical applications. TiO_2 and SiO_2 gel films are early induced sol–gel-derived biomedical films for Ti and Ti alloys, which is well known to facilitate the formation of bone-like apatite in SBF. For high density of hydroxyl groups in TiO_2 and SiO_2 gel films, calcium phosphate is induced on the surface of Ti implants as an enhanced bonding can form between –OH and calcium phosphate. Advincula et al.[497] compared the sol–gel TiO_2 and passivation methods for improving the bioactivity of Ti–6Al–4V and demonstrated that the sol–gel TiO_2 surface has a better mineralization ability and therefore better MC3T3-E1 cells proliferation. Liu et al.[498] prepared sol–gel TiO_2 film on TiNi alloy and found simultaneously enhanced corrosion resistance and blood biocompatibility. Yoshida et al.[499] synthesized thin sol–gel SiO_2 and SiO_2/F films on CP–Ti; their results showed that both films have a high bond strength (above 55 MPa) to the CP–Ti substrate and the films significantly reduce the release of Ti ions in 1 wt% lactic acid solution. Nevertheless, using TiO_2 and SiO_2 gel films still has a limited bioactivity. Some scholars proposed to directly synthesize calcium phosphate films on Ti and Ti alloys to improve their biocompatibility and bioactivity. Stoch et al.[500] successfully prepared HA sol–gel and deposited the sol–gel on Ti and Ti–6Al–4V by dipping. However, Piveteau et al.[501] pointed out that pure HA film prepared by sol–gel has a low adhesion strength to Ti substrate and therefore a transition layer is required. To solve such a key problem, Kim et al.[502] and Xu et al.[503] suggested to use HA/TiO_2 bi-layered film, which also can be synthesized by sol–gel. As shown in **Figure 12**a, a HA/TiO_2 bi-layered film is clearly attached on CP–Ti substrate. The HA/TiO_2 double-film coated CP–Ti exhibits enhanced bond strength (Figure 12b) as well as improved bioactivity. Due to the buffer layer of TiO_2, the sample also shows better corrosion resistance in physiological saline solution. In contrast, HA/TiO_2 composite films has also been suggested by Milella et al.[504] and Wen et al.[505]. Such composite films are prepared by mixing TiO_2–sol and HA–sol. Milella et al.[504] indicated that HA/TiO_2 composite film on CP–Ti has an adhesion strength of about 39.8 ± 3.75 MPa. Wen et al.[505] deposited HA/TiO_2 composite film on Ti–50Zr alloy and found the coated sample has an excellent bone-like apatite-forming ability in SBF. Other modified HA films, including fluor-HA,[506] hydrophilic calcium HA,[506] and silica-polyethylene glycol films,[507] have also been reported to improve the biocompatibility of Ti and Ti alloys. Furthermore, sol–gel method shows a relatively low processing temperature to synthesize various films on Ti and Ti alloys. Such combined advantages enable sol–gel method to have high potential for a variety of industrial applications.

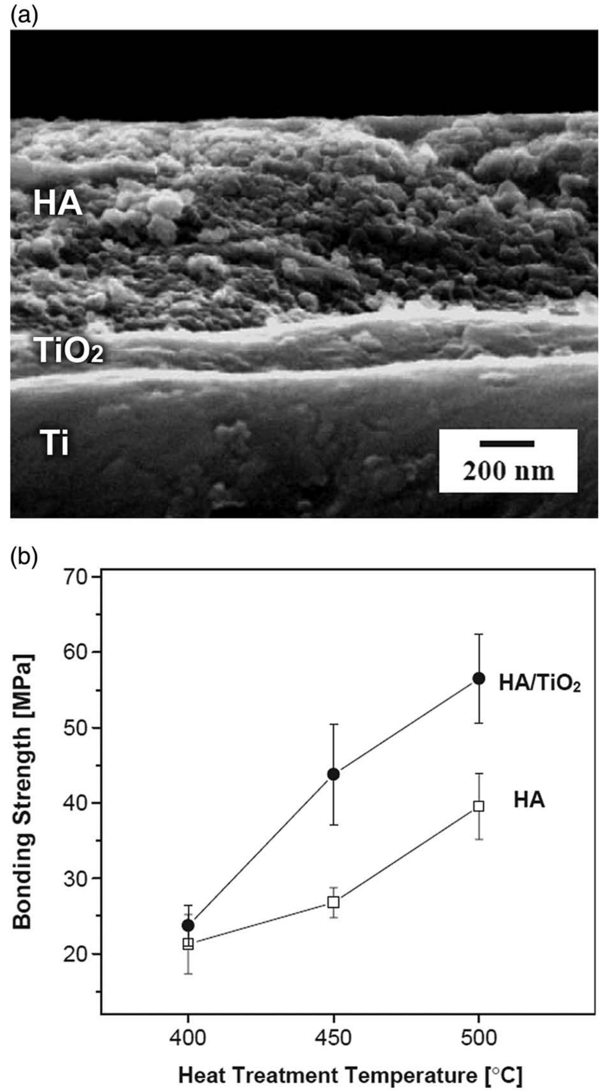

Figure 12. a) Cross-sectional microstructure and b) bond strength of HA/TiO_2 double films. (Reproduced with permission.[502] Copyright 2004, Elsevier).

3.3.3. Chemical Vapor Deposition

In comparison to PVD methods, CVD deposits films on metallic materials depending on the chemical reactions between components in the gas phases and volatile components on the substrate surface.[508,509] According to their working conditions, CVD techniques can be categorized into plasma-enhanced CVD,[510] laser-enhanced CVD,[511] atmospheric-pressure CVD[512], low-pressure CVD,[513] and aerosol assisted CVD.[514] CVD has a better capability to synthesize thin films with higher coverage compared with PVD. CVD also can coat workpieces with complex shapes and it is commonly used to enhance the mechanical and biological properties of Ti and Ti alloys. TiN, TiC, TiC_xN_{1-x}, and even DLC films have been frequently used. TiN, TiC, TiSiN, and TiCN can be synthesized using the volatile $TiCl_4$ precursor and the reactant gases of N_2, H_2, SiH_4, CH_4, etc., at a high temperature.[161,515,516] Such Ti-based films exhibit extremely high hardness (up to 100 GPa) and wear resistance compared with Ti substrate. Movassagh-Alanagh et al.[516] found TiSiN coated Ti–6Al–4V not only has an improved wear resistance but also an enhanced corrosion resistance in SBF. Yilbas et al.[517] obtained similar results from TiN coated Ti–6Al–4V. It was reported that such Ti-based films can reduce the ion release due to the enhanced corrosion resistance of the coated Ti and Ti alloys, leading to an increase in biocompatibility.[518,519] Meanwhile, due to the combination advantages of extremely high hardness, low friction coefficient, superior corrosion resistance, DLC films are introduced to Ti and Ti alloys. Rats et al.[520] and Chandra et al.[521] prepared DLC films on CP–Ti and Ti–6Al–4V. However, because of the large difference in thermal expansion coefficients between Ti ($8.8 \times 10^{-6}\,°C^{-1}$) and CVD diamond ($1.1 \times 10^{-6}\,°C^{-1}$), a considerably large compressive stress (up to 7 GPa in magnitude) is generated in the film.[520] Such a high residual stress may cause the debonding of DLC film from Ti substrate.[520] To reduce the internal stress, a buffer layer of TiC is always induced during CVD processing.[522] The DLC-coated Ti–6Al–4V alloys show a higher hardness and an enhanced wear resistance compared with uncoated counterpart.[523] As shown in **Figure 13**, CVD-prepared DLC film has comparable wear resistance with magnetron-sputtered Ti–MoS_2.[523] However, CVD has a high processing rate than magnetron sputtering. Therefore, CVD–DLC becomes a better choice for turbine engine application due to its high efficiency and good property. On the other hand, DLC films have promising oxidation resistance.[524] Although rare research has reported on the thermal stability of DLC-film coated Ti and Ti alloys, it is believed that DLC films are also suitable for Ti and Ti alloys for moderate- or high-temperature applications. The biocompatibility of DLC-film coated Ti and Ti alloys has been widely investigated. Jones et al.[519] pointed out that DLC film has a comparative hemocompatibility with TiC and TiN films in accordance with platelet attachment and hemoglobin levels tests. Meanwhile, DLC film shows a slightly better fibrinogen protein adsorption than TiC and TiN films.[451] Mohanty et al.[525] conducted in vivo test in rabbits using DLC-coated CP–Ti and uncoated CP–Ti. Long-term implantation results indicated both DLC-coated CP–Ti and uncoated CP–Ti are compatible with skeletal muscle, whereas DLC-coated CP–Ti exhibits higher wear resistance and corrosion resistance than uncoated CP–Ti. Combining these advantages, DLC films also have high potential for biomedical applications.

Finally, the disadvantages of CVD are also apparent. For instance, the required CVD operating temperature is too high to process the deformed or metastable Ti and Ti alloys. Processing at a high temperature may sacrifice the mechanical properties of such deformed or metastable Ti and Ti alloys. In the meantime, as the chemical reactions in CVD take place in gas phase, nonvolatile components could not be used, which restricts the variety of the resultant products. Furthermore, the deposition rate of CVD is extremely low and the remnant of reaction gas may be toxic or explosive.[161] Therefore, CVD still has a narrower application fields compared with PVD.

3.4. Biochemical Method and Drug-Loaded Method

Biochemical method and drug-loaded method for Ti and Ti alloys are merely used in the biomedical applications, which aims to improve their bioactivity, biocompatibility, and/or antibacterial functions. For such purposes, the immobilization of extracellular matrix (ECM) proteins and/or incorporation of antibiotics on the surface of Ti implants are investigated thoroughly. The former usually immobilize ECM proteins and short biomimetic peptides on implant surfaces. Among all ECM proteins, collagen is the most promising one for protein immobilization.[240] Generally, the Ti samples are first deposited by amino groups which are produced by allylamine plasma.[240] This method can introduce both primary and secondary amino groups on the Ti substrate.[240] Amino groups can enhance the bioconjugation reactions and improve the potential for grafting bioactive molecules due to their high reactivity to *N*-hydroxysuccinimide.[526,527] After deposition of amino groups, Ti samples are then immersed in a collagen solution at 37 °C for about 8 h. After immersion, the collagen solution is displaced by phosphate buffer solution which contains water-soluble carbodiimide and *N*-hydroxysuccinimide.[240] As such, covalent linking between Ti substrate and collagen is formed. Morra et al.[528] found that human mesenchymal cells (HMC) are stimulated by collagen on the coated CP–Ti and the density of HMCs increases quickly in a short period. In vivo studies also show many successful outcomes of collagen. Sverzut et al.[529] implanted 12 collagen coated CP–Ti implants and 12 uncoated counterparts in the mandibles of 6 mongrel dogs for 3–8 weeks; their results showed a higher level and higher expression of genes-encoded alkaline phosphatase adjacent to collagen-coated implants.

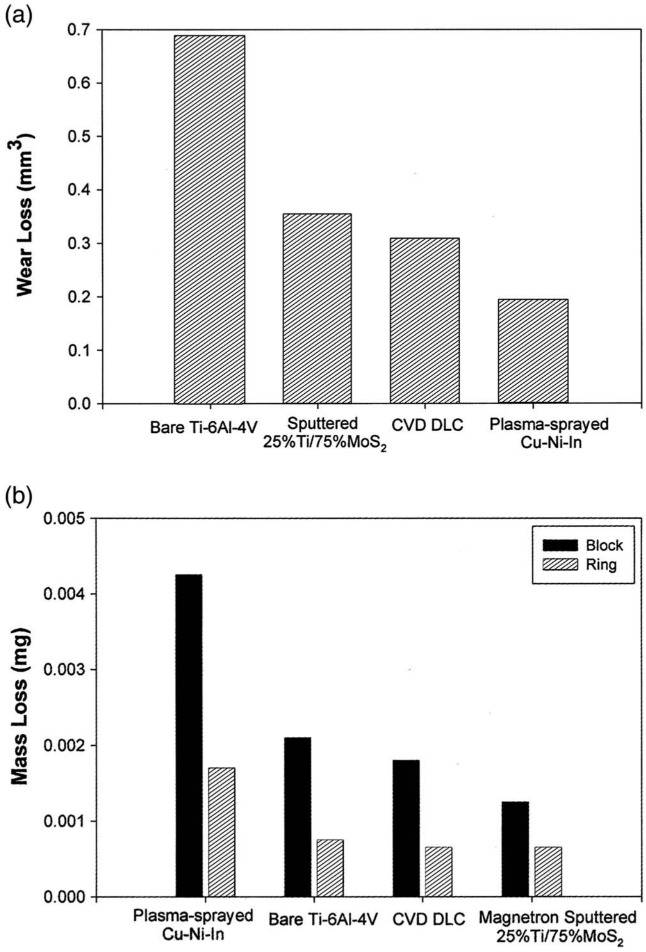

Figure 13. Tribology properties of bare and coated Ti–6Al–4V: a) wear volume loss and b) mass loss obtained from block-on-ring tests. (Reproduced with permission.[523] Copyright 2000, Elsevier).

Moreover, peptides, especially short biomimetic peptides, are reported to be highly bioactive. However, the Ti substrates are "bioinert" in nature and cannot have a good conjunction with bioactive molecules (such as peptides and proteins). Therefore, they should be treated before the immobilization of peptides. As seen from Section 2.2.2, plasma polymerization is a common method to activate the Ti surface.[530,531] Hoene et al.[530] investigated the inflammatory response of allylamine plasma polymer-coated CP–Ti in a rat model and found that the coated samples have comparable local inflammation response to the controls. Therefore, plasma polymerization, especially the ammonia plasma treatment, is always used before the immobilization of peptides. Among the biomimetic peptides, short biomimetic peptides are cheaper and prone to be produced in higher purity and better stability compared with other types of peptides.[532] Tripeptide Arg-Gly-Asp (RGD) is most frequently used short biomimetic peptide and it is derived from fibronectin and vitronectin. This type of peptide shows a great positive influence on cell adhesion. Dettin et al.[532] demonstrated that tripeptide RGD can increase the adhesion of osteoblast-like cells. Due to their relatively small size, it is possible to control the peptide orientation on approach to a Ti surface, which enables the favorable presentation of bioactive motifs. Martin et al.[533] demonstrated that the peptide orientation and their surface concentration can be controlled by adjusting the solution pH or using an electric field by a battery. These findings shed light on the mechanisms of biomolecule immobilization and provide a promising solution to the design of synthetic peptides and advanced biofunctionalized materials. Some peptides have biomimetic functions. Such functions can impart the implants after immobilization. Seol et al.[534] used a synthetic peptide to mimic bone morphogenetic protein-2 (BMP2). Before immobilization, the Ti samples were immersed in a 2% stirring hexane solution for 30 min under Ar bubbling to activate its surface. The treated samples were then reacted with the heterobifunctional crosslinker for 2 h. Afterward, the samples were washed and reacted with 2 mg per 0.5 mL synthetic peptide in phosphate-buffered saline. As such, chemical immobilization of synthetic peptides onto Ti samples was conducted. Both in vitro and in vivo tests showed a higher growth rate of the MC3T3-E1 cells on the immobilized CP–Ti compared with the untreated counterpart. Although these methods are used for protein adsorption, protein adsorption may be deleterious in some cases, e.g., stents and sensors. Therefore, protein-resistant methods emerged. For instance, a simple method to reduce the protein adsorption is to synthesize an inert protein coating on the implants (devices), e.g., albumin.[535] Meanwhile, Tosatti et al.[536] investigated the graft copolymer poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) and its derivatives on the surface of Ti-coated Si wafer samples by a simple dipping process and their outcomes indicated that almost no proteins adsorption is present on all coated samples after incubation in heparinized blood plasma for 1 h. Due to the good protein resistance, Khoo et al.[537] elucidated that the modified PEG has antibacterial function. They synthesized multivalent Ti-binding peptides poly(ethylene glycol) (TBP-PEG) conjugates which show a relatively high stability in serum after 2 weeks, as shown in **Figure 14**a. The stability increases with increasing the number of TBPs, leading to an opposite effect of the formation of biofilm (Figure 14b) and the bacteria attachment (Figure 14c). In addition to the biochemical methods, drug-loaded methods are often used for antibacterial function, which primarily focuses on the broad-spectrum antibiotics, such as gentamicin, cephalothin, carbenicillin, simvastatin, tobramycin, and vancomycin.[538–540] Such antibiotics are not directly coated on the surface of Ti and Ti alloys but incorporated in the other coatings, including HA, biodegradable polymers, and sol-gel films. Some studies indicated that the antibiotic-incorporated coatings on Ti implants significantly decrease the attachment of *Staphylococcus aureus* in both in vitro and in vivo experiments.[541,542] However, some issues, such as microbial resistant and cell toxicity, should be concerned.[540,543,544] Therefore, one should still use antibiotics with caution. Finally, it is worthy to point out that both biochemical and drug-loaded methods can be combined with other surface-modification methods to obtain multifunctional coatings for biomedical applications.

4. Comparison and the Future Interests of the Surface Modifications for Ti and Ti Alloys

As there exists a considerable number of surface-modification technologies for Ti and Ti alloys, it is vital to select appropriate ones for their specific applications. The appropriate surface modification could retain the great properties of underlying bulk Ti substrates as well as improve their surface properties required in different environments. Meanwhile, the surface-modified layers should have adequate bond strength to the substrate. **Table 4** summarizes various surface-modification technologies and the characteristics of their modified layers, which can be a guidance for choosing appropriate technology used for different application purposes. By and large, surface-modified layers have better wear resistance, fatigue resistance, corrosion resistance, bioactivity, or biofunctionability compared with unmodified Ti and Ti alloys.

It is well known that the wear resistance of coatings materials is basically determined by the microhardness and elastic modulus. A higher ratio of hardness to elastic modulus generally indicates better wear resistance because the plastic deformation is reduced during friction.[61,568] Based on this consideration, the hardness and elastic modulus of coating materials prepared by different surface-modification technologies are summarized in **Figure 15**, where TiXN means Ti-X-N ternary compounds (*X* indicates the other elements, such as C, Al, Si, and so on). As mentioned earlier, the coating materials with a higher hardness but lower elastic modulus may lead to better wear resistance. After a simple comparison, ZrO_2, TiC, TiXN (such as TiCN, TiAlN, and TiSiN) and DLC layers may have better wear resistance than others. Furthermore, fatigue resistance is also a critical consideration for Ti and Ti alloys used as loading workpieces, such as artificial joints and engineer blades. Generally, the materials with higher yield strength possess better fatigue resistance.[194,195] Although many surface-modified layers exhibit higher yield strength than Ti and Ti alloys, delamination is prone to take place due to the large differences in elastic moduli of the surface-modified layers and the substrate. As such, surface nanocrystallization methods (such as FSP and SMAT) become the prior choice because they can significantly improve the surface strength and therefore their fatigue resistance of Ti and Ti alloys.[159,352,353,364,365,545] These methods induce an inherent gradient layer at the surface of Ti and Ti alloys. Hence, no

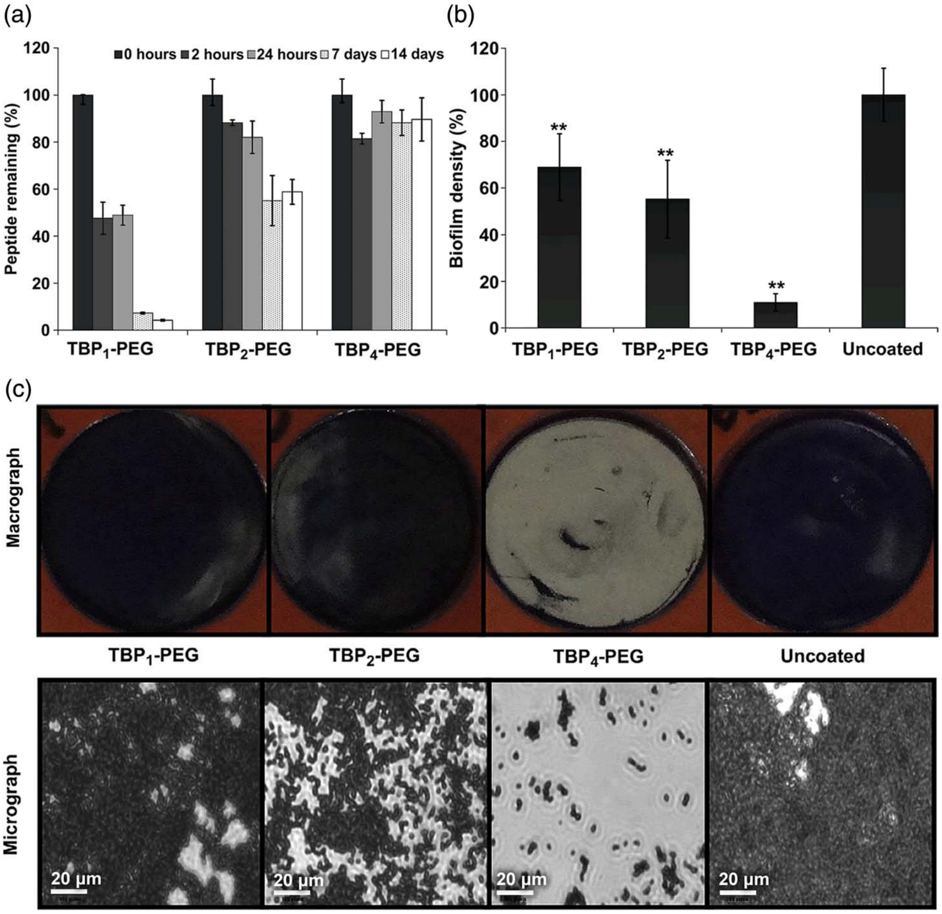

Figure 14. In vitro results of TBP-PEG conjugates coated CP–Ti and uncoated counterpart: a) exposure to 100% human serum over 2 weeks, b) biofilm formation, and c) macrograph photographs and phase-contrast micrographs after 5 h exposure to *Staphylococcus aureus*. The number in sample name indicates the number of TBP. TBP-PEG means Ti-binding peptides poly(ethylene glycol). (Reproduced with permission.[537] Copyright 2010, Elsevier).

delamination would take place even under repeated loading condition. However, the refined grains in this inherent gradient layer can be easily coarsened at high temperature, resulting in decline in their properties. Therefore, thermal barriers (such as ZrO_2 and DLC coatings) are often required and synthesized on the surface of Ti and Ti alloys by thermal spraying or CVD (Table 4). Although such thermal barriers could not meet all requirements for Ti and Ti alloys in high-temperature environment, their service lives are substantially extended.

Corrosion is one of critical considerations for structural materials in service. Essentially, the corrosion of a metallic material is attributed to the loss of electrons of metallic atoms. Afterward, the metallic atoms become cations which would be dissolved in a corrosive environment.[168,569] For Ti and Ti alloys, the dissolved Ti atoms can form a passive film (mainly consisting of TiO_2) by reacting with OH^- to protect the underlying substrate from further corrosion. Therefore, Ti and Ti alloys possess good corrosion resistance.[6] However, most surface-modified layers show better corrosion resistance than Ti and Ti alloys. There are two reasons accounting for this phenomenon. On one hand, most surface-modified layers are ionic or covalent compounds. Ionic bonding or covalent bonding are much stronger than metallic bonding. Therefore, the surface-modified layers always have higher corrosion potentials than Ti and Ti alloys.[374,382,416] In contrast, Ti and Ti alloys with refined microstructure contain a larger number of grain boundaries, which is primarily confined to control the rate of anodic reactions.[568] Therefore, Ti and Ti alloys with refined grains often possess better corrosion resistance.[349,568] Improved corrosion resistance can render Ti and Ti alloys to be used in marine industry and also reduce their ion release when used as implant in the human body. Understanding these two factors is favorable to select proper surface-modified layers for the corrosion-resistant applications.

Another important application for Ti and Ti alloys is bone replacement. Bioactivity can determine the success of the implantations. As such, various bioassays are used in many previous studies.[483,484,498] To give a relatively objective comparison among different types of surface-modified layers, increased bioactivity, which was derived from the comparison of bioassay on bare CP–Ti surface and corresponding surface-modified layer for MG63 cell adhesion, is selected as shown in **Figure 16**. As there are a variety of peptides, including short biomimetic peptides, growth factors and so on, the data for the bioactivity of various peptides as shown in Figure 16 are presented in a single

Table 4. Comparison of various surface modifications and the characteristics of their modified layers.

Surface modification technology	Applications	Processing rate	Modified layer	Thickness	Relative density	Bond strength	Ref.
Mechanical methods							
Grind and polish	To remove contamination / deformation layer and obtain a low roughness surface	N.A.[a]	Smooth surface	N.A.	N.A.	N.A.	[180,181]
Sandblasting	To remove contamination / plastic deformation layer and obtain an acceptable surface with a certain roughness or a specific topography	N.A.	Severe deformation layer with specific topography	≈0.5–1 μm	Full density	Very high	[182,183]
Shot peening	To improve hardness, wear resistance, corrosion resistance and fatigue resistance	≈5–60 s	Severe deformation layer with specific topography	≈100–300 μm	Full density	Very high	[159,545]
Friction stir processing	To improve hardness, wear resistance, and biocompatibility	500–750 mm^2 min^{-1}	Severe deformation layer (incorporation of other particles, such as TiO$_2$, Ag and Zn)	Up to 1 mm	Full density	Very high	[352,353]
Surface mechanical attrition treatment	To improve hardness, wear resistance, fatigue resistance corrosion resistance and biocompatibility	≈15–60 min	Nanocrystalline work-hardened surface layer	≈10–200 μm	Full density	Very high	[364,365]
Physical methods							
Thermal spraying	Improve wear resistance and biocompatibility; or to be thermal barrier coatings	≈2–20 kg h^{-1}	Metallic, ceramic and composite coatings, such as Ni, Al$_2$O$_3$, hydroxyapatite, etc.	Several microns to several millimeters	≈∼80–98%	20–80 MPa	[162,546–548]
Plasma surface modification	Clean and sterilize surface; remove native oxide layer and increase the surface energy	N.A.	Oxide layer dominated by TiO$_2$ with lower carbon contamination	≈0.5–2.5 nm	N.A.	N.A.	[224,228]
Plasma deposition (solid targets and plasma gas are available)	Improve hardness, wear resistance, corrosion resistances, fatigue limit and biocompatibility	≈30–40 nm min^{-1} in thickness	TiO$_2$, TiN, TiOH, TiCN layers	≈2–150 nm	Nearly full density	N.A.	[229,237]
Plasma polymerization	To produce an active surface for better immobilization of bioactive molecules	Several seconds to dozens of minutes	Modified surface with amino groups	Monolayer	N.A.	N.A.	[233,241,243,247]
Ion implantation and deposition	To improve hardness, wear resistance, fatigue resistance, corrosion resistance and blood compatibility	N.A.	Surface-modified layer and/or thin film, such as Ti–O, Ti–N films	0.01–1 μm	Full density	Very high	[549–551]

Table 4. Continued.

Surface modification technology	Applications	Processing rate	Modified layer	Thickness	Relative density	Bond strength	Ref.
Laser surface remelting	To improve hardness, wear resistance, and corrosion resistance	$\approx$0.1–25 $mm^2 s^{-1}$	A martensite layer covered with TiO_2	Totally, up to 100 μm;	Full density	Very high	[409,552]
Laser surface alloying	To improve hardness, wear resistance, oxidation resistance, and corrosion resistance	$\approx$20–115 $mm^2 s^{-1}$	Alloyed layers which may contain TiN, TiC, Al_2O_3, etc. depending on the additives used	$\approx$0.5–1.0 mm	Full density	Moderate	[417–420]
Laser cladding	To improve hardness, wear resistance, oxidation resistance, corrosion resistance and biocompatibility	$\approx$12–140 $mm^2 s^{-1}$	Metal, composite and ceramic coatings such as NiCoCrAlY, Ti-Al, Ti-Ni, hydroxyapatite etc.	$\approx$0.005–1 mm	Nearly full density	Moderate	[435,553]
Evaporation plating	To improve hardness, wear resistance, corrosion resistance and biocompatibility	$\approx$10–25 000 nm min^{-1} in thickness	Metals and compound films, such as TiO_2, TiN, TiC etc.	Up to 5 μm	Nearly full density	Moderate	[442,443]
Ion plating	To improve hardness, wear resistance, corrosion resistance and biocompatibility	$\approx$10–25 000 nm min^{-1} in thickness	TiN, TiC, TiCN, DLC and amorphous carbon films	Up to 3 μm	Full density	Moderate	[444,447]
Sputtering (e.g., RF sputtering and magnetron sputtering)	To improve hardness, wear resistance, corrosion resistance and biocompatibility	$\approx$25–1000 nm min^{-1} in thickness	In addition to the films prepared evaporation plating and ion plating, some ceramic and refractory metal films are available	Up to 4 μm	Nearly full density	Moderate	[461,462]
Chemical methods							
Pickling	To remove contamination / deformation layer / oxide scale	$\approx$0.2–10 nm min^{-1} in thickness	Oxide layer dominated by TiO_2	$<$10 nm	N.A.	N.A.	[250,251,253]
Alkali treatment	To produce specific topography and improve bioactivity	$\approx$0.7–3.33 nm min^{-1} in thickness	Sodium titanate gel	$\approx$1 μm	Porous	Very high	[262,263,265]
Passivation treatment	To obtain a uniform oxide layer for the purpose of enhancing corrosion resistance and wear resistance	$\approx$5–10 nm min^{-1}	Oxide layer dominated by TiO_2	$\approx$2–30 nm	Full density	High	[265,275]
Hydrogen peroxide treatment	Improve biocompatibility or bioactivity	$\approx$0.17–0.33 nm min^{-1} (inner layer)	Ti–peroxyl gels	Inner oxide layer $<$ 10 nm; outer porous oxide layer up to 40 nm	N.A.	High	[554,555]
Electropolishing	To obtain a reproducible and well-defined commencement for subsequent other surface treatments	1–10 μm min^{-1} in thickness	A smooth surface with almost no contamination	N.A.	Full density	N.A.	[290,291]

Table 4. Continued.

Surface modification technology	Applications	Processing rate	Modified layer	Thickness	Relative density	Bond strength	Ref.
Anodic oxidation	To obtain improved adhesive bonding, corrosion resistance, and coloration and to produce specific surface topographies	1.9–6 nm V^{-1} in thickness	Oxide layer dominated by TiO_2 (incorporation of electrolyte ions)	≈10–100 nm	Full density	29–42 MPa	[180,185,556–558]
Electrodeposition and electroplating	To improve hardness, wear resistance, corrosion resistance, oxidation resistance, biocompatibility and bioactivity	≈2–20 μm min^{-1}	Metallic and non-metallic coatings, such as Cu, Al_2O_3, hydroxyapatite, and composite coatings	Up to 200 μm	Nearly full density	15–40 MPa	[312,327,559]
Micro-arc oxidation	Significant improvement in biocompatibility and bioactivity	≈1–3 μm min^{-1} in thickness	Porous oxide coating dominated by TiO_2 (incorporation of electrolyte ions)	Up to 40 μm	Porous	5–44 MPa	[487,560–562]
Sol-gel	Highly homogeneity and improvement in bioactivity.	Several steps for the preparation of sol-gel, transfer of sol-gel to substrate, aging and drying	Gel films such as titanium dioxide, silicon dioxide, calcium phosphate and composite	Up to 28 μm	High	3–55 MPa	[501,502,504,563,564]
Chemical vapor deposition	Improve wear resistance, corrosion resistance and biocompatibility; potential for mild- or high-temperature applications	Deposition films by chemical reaction at a high temperature	TiO_2, TiN, TiOH, TiCN, TiSiN and diamond-like carbon thin film	≈1 μm	Nearly full density	N.A.	[524,565]
Biochemical and drug-loaded methods							
Biochemical method	Improve bioactivity and biocompatibility	Soaking in the proteins- or peptides- containing solution for 6–12 h	Immobilization of proteins and short biomimetic peptides	Up to 0.1 nmol cm^{-2}	N.A.	N.A.	[540,566,567]
Drug-loaded methods	To obtain antibacterial function, but also may cause microbial resistant and cell toxicity	N.A.	Antibiotics, such as gentamicin, cephalothin, and vancomycin, loaded in the other coatings, including hydroxyapatite, biodegradable polymers and sol-gel films	N.A.	Depending on the coatings used	N.A.	[540,541]

[a] N.A. means not available.

cylinder bar to give a simple comparison to the other surface-modified layers. As such, the data for the bioactivity of various peptides span a large range. Apparently, collagen and peptide exhibit better bioactivity for MG63 compared with other surface-modified layers. Such a finding illustrates that human osteoblast-like cells can be chemically stimulated. Similar results were also found for HMCs.[528] However, collagen and peptide have no contributions to the wear resistance and corrosion resistance of the Ti substrate. Hence, Ti and Ti alloys with simple collagen or peptide layers may still have poor wear resistance. Fortunately, immobilizing collagen, peptide, or other proteins can be conducted on the other surface-modified layers, such as electrolytic deposition layers,[570] sandblasted surface,[571] HA coatings,[572] and so on. Therefore, using a wear- and corrosion-resistant inner layer and a bioactive layer to coat the surface of Ti and Ti alloys may be a promising method in the

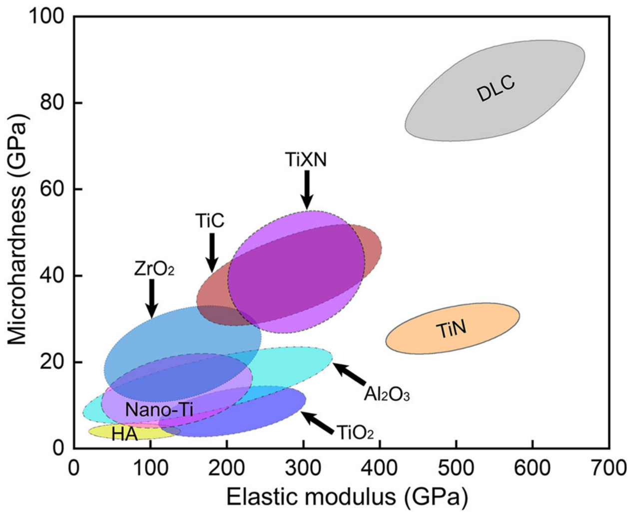

Figure 15. Microhardness and elastic modulus of coating materials prepared by several surface-modification methods. TiXN means Ti-X-N ternary compounds, where *X* indicates the other elements, such as C, Al, Si, and so on. HA means hydroxyapatite and DLC indicates diamond-like carbon.

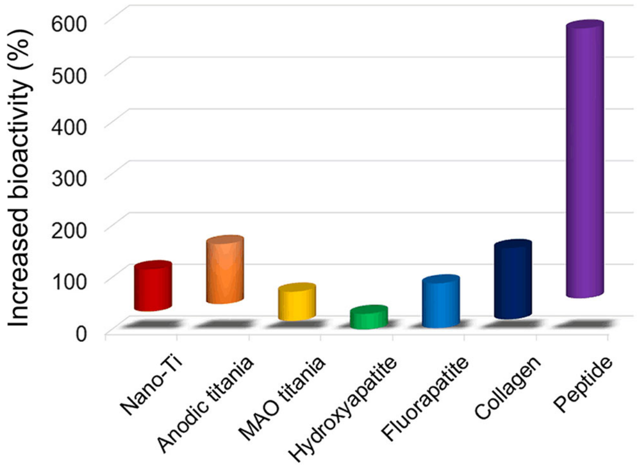

Figure 16. Increased bioactivity derived from the comparison of untreated CP–Ti surface and various surface-modified layers using human osteoblast-like cells (MG63). MAO means micro-arc oxidation.

future. The substrate underlying may also influence the bioactivity and biocompatibility of the surface-modified layers as different types of Ti alloys have different chemical compositions. Meanwhile, this issue may be more complex due to the interactions between the different external conditions (such as electrolyte, sol-gel, and feedstock) and different substrates. Therefore, few studies have been carried out to compare the bioactivity and biocompatibility of the surface-modified layers using different Ti substrates. From another point of view, if the surface-modified layers are "added" to the Ti substrates, the underlying substrate can be almost isolated by the surface-modified layers. If the surface-modified layers are processed by the underlying substrates (such as FSP, SP, and SMAT), the bioactivity and biocompatibility of the surface-modified layers still strongly depend on the substrate used.

The requirements of surface properties may be higher and higher in the future, which demands the further development of surface-modification methods. Up to date, although all surface-modification methods are still presented in laboratory research or industrial application, the distinctions in these methods are also evident. Some methods possess higher surface-modification rate (such as laser surface modification and thermal spraying), the capability to coat the complex-shape objects (such as sol-gel, electrodeposition, anodic oxidation, and ion implantation) or high-performance modified layers (such as PVD, FSP, SMAT, and so on). Some conventional methods (such as grinding, polishing, pickling, and sandblasting) may not have the ability to significantly improve the surface properties of Ti and Ti alloys, but they can often be used as pretreatments for other surface-modification methods. Some biological methods (such as biochemical method and drug-loaded method) can be used as post-treatments in the biomedical applications. Sole surface-modification method may be seldom used in the coming years. For instance, sandblasting is always used before spraying to increase the surface roughness of the substrate to improve the coating bond strength.[211] In comparison, the surface of substrate should be ground and polished to decrease the surface roughness and remove the surface contamination. In such a situation, the surface of substrate becomes clean and smooth and therefore many surface modifications (such as chemical, electrochemical, and sol-gel methods) can be conducted.[185,186] Yilbas et al.[573] found that PVD-deposited TiN on laser nitrided Ti–6V–4V has higher bond strength and shear strength than that on the untreated Ti–6V–4V. PSed thermal barriers have low bond strength to Ti substrate, whereas PVD-prepared thermal barriers have low oxidation resistance. Therefore, PSed PVD was developed in the 1990s to couple the advantages of both PS and PVD.[574] Moreover, to satisfy the requirements of industry manufacturing and to obtain better performance, future interests of the surface-modification methods for Ti and Ti alloys can be concluded based on the review. For example, incorporating other powder can render more functions of the surface-modified layers on Ti and Ti alloys after the FSP. Hence, the uniform distribution of the incorporating powder, which is related to the design of powder groove and the viscoplastic fluid behavior of Ti substrate, is vital to the development of FSP technology. Another surface nanocrystallization method, namely, SMAT exhibits a lot of advantages, including universality, high tenacity, and good bonded interface. In the future, to develop practical equipment in the manufacturing industry and to improve the stability of the surface, nanocrystallization will become the main task for SMAT. Laser surface treatment, especially laser cladding, is a promising technology due to its versatility in various applications. In the next stage, optimizing the processing parameters of laser processing, controlling the cracks in the laser-treated surface-modified layers, and adopting ultrashort pulse laser equipment are the future interests for this technology. For MAO, decreasing the cost by increasing the utilization of energy and building a better discharge model and film growth model are needed. In addition to the preparation methods, the performance of modified layer also strongly depends on the coating materials (Figure 15 and 16). More newer coating materials with higher performance are required urgently. Therefore, it can be expected that multiple emerging surface-modification methods with higher-performance modified layers would be used in the future to achieve better properties and broader applications for Ti and Ti alloys.

5. Conclusions

This article reviews a variety of surface-modification methods with aim to improve the mechanical, corrosion, and biological properties of Ti and Ti alloys. Although Ti and Ti alloys possess many fascinating properties (including high specific strength, high corrosion resistance, and biocompatibility) and have been used in various industries, some problems are still encountered on their surfaces during service. As such, surface modifications are conducted on the surfaces of Ti and Ti alloys to synthesize protective- or biological-modified layers to ensure their duration and reliability in the service environments.

In terms of the formation mechanism of surface-modified layers, conventional methods are generally classified into mechanical, physical, chemical, and biochemical methods. Some conventional methods, such as sandblasting, thermal spraying, alkali treatment and glow discharge plasma treatment, have limited improvement in the surface properties or restriction on the geometry of workpieces. Therefore, many advanced surface-modification technologies, such as FSP, SMAT, laser surface modification, MAO, PVD, and so on, have emerged in the recent decades. These advanced surface-modification methods make Ti and Ti alloys exhibit better performance and have extended applications.

Although various surface-modification methods can improve the properties of Ti and Ti alloys to a large extent, further investigations are still required. With the higher requirement of surface properties in the future, surface-modification methods are also needed to be further advanced. To advance the current technologies, deep understanding of the mechanism in surface modification is necessary. Meanwhile, incorporation of different surface-modification technologies (e.g., plasma spray-PVD or using one surface-modification method as a pretreatment before another technology) may be widely used in the future. In addition, new coating materials with high performance are also required urgently. Therefore, incorporation of different surface-modification technologies with high-performance modified layers may be the mainstream of surface modifications for Ti and Ti alloys (and other metals as well), which is striving for high performance and broad applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioactivities, corrosion, surface modifications, titanium, wear resistances

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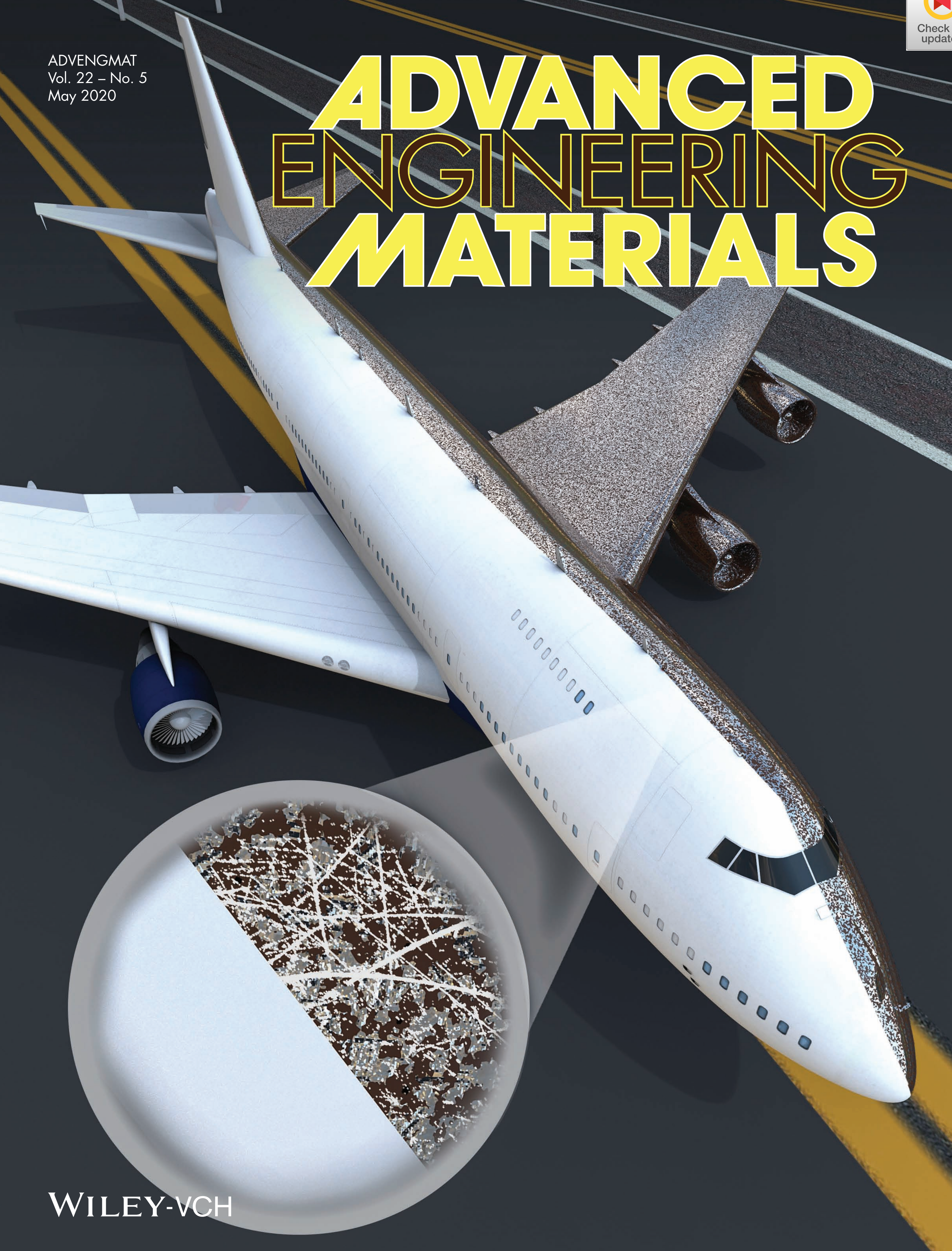

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